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Geology and Mineralogy
Åbo Akademi University
2013

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ISBN 978-952-12-2956-5
Painosalama Oy – Turku, Finland 2013

Abstract

The Larsmo-Öja Lake on the west coast of Finland was once a part of the inner archipelago of the Bothnian Bay, but was embanked at narrow straits for the industrial use of fresh water. Since the 1960s the area has been a fresh water reservoir. The lake is an estuary of four rivers and many small streams, and is an important spawning and nursing area for various fish species. Since the late 1960s the lake has often suffered from low pH (pH<5) and high metal concentrations with occasional fish kills. This has generated intensive debate because the lake is important for recreation, fisheries and industry. The embankment that prevents dilution and neutralization by brackish water has often been blamed for the water quality problems. This study investigates the underlying causes to the acidification, and the role of land use, hydrology and a possible climate change on the behavior of the load. Potential mitigation methods, and the effects on the ecology with fish larvae as a bio indicator, were also studied. Overall increased knowledge and awareness of the acid- and metal load in the area will help us improve the water quality in the future.

The embankments make the lake area undoubtedly more sensitive to the acidic load, but the primary cause to the decline in the water quality in the late 1960s occurred because the decline in water quality also took place in the rivers discharging into the Larsmo-Öja Lake. The decline in water quality at this period also occurred in many other rivers in western Finland, and was due to intensified land use in the river valleys that are commonly underlain by sulfidic sediments. This led to the formation of acid sulfate (a.s.) soils and a heavy discharge of acidity and metals.

According to this study, the a.s. soils in the catchment area of the Larsmo-Öja Lake are very heterogeneous in grain size, depth and sulfur concentrations compared to other a.s. soils in western Finland. Discharge from these soils cause the low-order streams and four rivers discharging into Larsmo-Öja Lake to carry acidity and metal concentrations on a yearly basis that far exceeds the background levels in Finland. Thus, the ecological status in both rivers and the lake is poor. Rough calculations show that sulfuric acid in the order of 65,000 tons, together with highly elevated concentrations of dissolved metals (such as aluminum), may reach the Larsmo-Öja Lake every year. The small streams draining directly into the lake drain only 7% of the catchment, but they contribute with an unexpected high share of the load; about one fourth of the total sulfuric acid and about one third of the metal load. The acidic load from dredge spoils and humic acids from forest- and peat lands, other much discussed reasons for acidification, proved to be insignificant to the lake as a whole.

The acidic metal discharge is very dependent on the hydrological conditions, and varies greatly between seasons and years; snow melt and intensive autumn rains cause the majority of the acidic metal discharge. Even though a dry summer is expected to cause increased sulfide oxidation with

intensified acidic events the following autumn, no such automatic response in water quality is found in this study. Instead, sufficient runoff during the autumn is more decisive in the severity of acidic events. Enhanced acidic events after a summer drought generally take place with a delay spanning several years, and several subsequent summer droughts seem to cause a cumulative effect. The present models of climate change expect warmer and rainier winters with increased runoff. This may already be visible in the study area, seen in increased acidity during the wintertime in the 2000s. Since the study area is already under heavy influence from acidity and metals, this may lead to further deterioration in the ecological and chemical status.

Since the worst years in the early 1970s the main river discharging into the lake, the Esse River, has shown a slight recovery in pH, probably due to the ongoing depletion of acidity in existing a.s. soils. In the recipient Larsmo-Öja Lake, where data was available from 1975, the 1980s seemed to be most acidic, but the improvement in pH in the Esse River does not seem to affect the lake. This may be due to increased acidic metal discharge from the smaller rivers and low-order streams.

Although estuary environments are important areas for the reproduction of coastal fish stocks, they are at the same time susceptible to the acidic metal discharge carried by the rivers. Due to the episodic nature of the acidic metal discharge, a full understanding of the consequences is difficult to obtain with only sporadic water sampling. In this study, the simple method of observing the occurrence of burbot (*Lota lota* L.) larvae gave comparable results on water quality to frequent water sampling over several months. The vast data series on the water quality from the Larsmo-Öja Lake shows that circumstances that may be detrimental to the production of burbot larvae have occurred almost every third year since 1975. The often occurring less severe acidic events are apparently intensive enough to be able to cause a frequent failure in the production of fish offspring, which probably have larger consequences in the long run than the relatively rare severe acidic events with spectacular kills on adult fish. Monitoring the larval community could therefore act as a reliable indicator on the effects on land use on water quality and coastal fish stocks in areas with a.s. soils.

To date, there are unfortunately no easy actions to take for the rapid improvement of water quality in areas with a.s. soils. Directing the outflow from the Larsmo-Öja Lake only through the southern outlet in order to save the northern part is motivated as a local first-aid measure, but it is notable that the acidic metal load is thereby only re-directed, and the rivers and the area outside the embankments do not directly benefit by this. Furthermore, the liming of watercourses is very difficult mainly due to the high quantities of lime required. Installation of controlled sub surface pipe-drains on already existing a.s. soils should, in theory, lower the environmental impact. However, it is unclear if the method has any effects in practice on the ground water level. The technique was therefore tested together with plastic sheets

below the ground to prevent by-pass flow, and showed potential in being able to avoid increased environmental impact even though the drainage efficiency increased. The most effective way to decrease environmental damage is to avoid the draining of sulfidic sediments as far as possible.

Consistent data are important in the study of long-term trends in water quality. Therefore, the current monitoring programs for many water courses that often show an unfortunate irregularity should be updated. The use of bio indicators was shown to be useful when investigating the short-term behavior and consequences of the acidic metal discharge in the absence of sufficient data on water quality. Consequently, appropriate monitoring, better knowledge of the causes, including a changing climate, and subsequent effects on ecology, together with proper studies of mitigation methods, will enable the application of more effective measures for mitigation in the future.

Sammanfattning

Larsmo-Öjasjön ligger vid kusten i västra Finland, och var tidigare en del av bottenvikens inre skärgård. Vägbankar och vallar byggdes vid smala sund p.g.a. industrins behov av färskvatten, och sedan 1960-talet har området varit en färskvattenreservoar. Fyra åar och ett stort antal diken och bäckar mynnar ut i sjön, som kan betraktas som ett stort estuarium. Sjön är ett viktigt förökningsområde för många fiskarter, och har ett högt rekreationsvärde. Sjön har fått uppmärksamhet pga. återkommande surchocker (pH<5) och höga metallhalter med fiskdöd som följd sedan slutet på 1960-talet. Invallningen, som hindrar brackvattnet från att späda ut och neutralisera det sura vattnet, har ofta beskyllts för problemen med vattenkvaliteten. Denna studie undersöker bakomliggande orsaker till försurningen samt påverkan från markanvändning, hydrologi och en potentiell klimatförändring. Effekterna på ekologin studeras med fiskyngel som bioindikator, och olika miljömetoder testas och diskuteras. Ökad kunskap om försurningen och metallproblemen hjälper oss att få förbättrad vattenkvalitet i framtiden.

Invallningen har gjort sjöområdet känsligare för försurningsproblem, men den primära orsaken till den dåliga vattenkvaliteten beror på att åarna som mynnar ut i sjön blev starkt försurade vid samma period som sjön, dvs. i slutet på 1960-talet, något som var typiskt i många åar i västra Finland. Detta berodde på att intensiva torrläggningsprojekt vid denna period företogs inom jord- och skogsbruket i de svavelrika sediment som är vanliga i ådalarna. Detta ledde till bildning av s.k. sura sulfatjordar med kraftig utsköljning av syra och metaller till vattendrag som resultat.

Denna avhandling visar att de sura sulfatjordarna i Larsmo-Öjasjöns tillrinningsområde varierar mycket i frågan om kornstorlek, djup och svavelhalt i jämförelse med andra sulfatjordar i västra Finland. Diken, bäckar och de fyra åarna som mynnar ut i sjön uppvisar mer eller mindre årligen syra- och metallhalter som klart överstiger bakgrundsvärden i Finland. Beräkningar visar att i klass med 65 000 ton svavelsyra tillsammans med stora mängder skadliga metaller i upplöst form, t.ex. aluminium, kan spolas ut i Larsmo-Öjasjön varje år, och detta orsakar permanent försämrat ekologiskt och kemiskt tillstånd i både åarna och sjön. Bäckarna och dikena som mynnar direkt ut i sjön dränerar endast 7 % av tillrinningsområdet, men bidrar med en oväntat hög andel av syra- och metallbelastningen; ca en fjärdedel av den totala syrabelastningen och en tredjedel av metallbelastningen. De talrika muddringarna i sjön och humussyror från skogs- och myrmarker, andra debatterade orsaker till försurningen, är obetydliga när det gäller helhetsbelastningen på sjön.

Syra- och metallbelastningen är mycket beroende av hydrologiska förhållanden, och varierar kraftigt mellan olika årstider och år. Största delen av belastningen sker under hög avrinning under snösmältning på våren och rikliga regn på hösten. I denna studie hittades inget direkt samband mellan en

torr sommar, som kan leda till intensifierad oxidering i sulfidleror, och försämrad vattenkvalitet följande höst. Avrinningens intensitet på hösten är däremot mera avgörande för surchockernas styrka. En torr sommar orsakar snarare en fördröjd effekt på vattenkvaliteten, och flera efterföljande torra somrar kan orsaka en kumulativ effekt som försämra vattenkvaliteten i flera år. Varmare vintrar med regn och ökad avrinning är att vänta i framtiden enligt de nuvarande modellerna för klimatförändringen. Detta fenomen kan stå bakom den ökade försurningen under vintern under 2000-talet, något som överlag kan förvärra den redan bräckliga situationen i studieområdet.

Sedan den värsta perioden i början på 1970-talet har Esse å visat en förbättring när det gäller pH-värdet. Detta beror troligtvis på en pågående urlakning av de existerande sura sulfatjordarna. I Larsmo-Öjasjön, där data finns tillgängligt först fr.o.m. 1975, verkade 1980-talet vara surast, men överlag syns ingen liknande förbättring i pH. Det faktum att förbättringen i Esse inte syns i Larsmo-Öjasjön kan bero på att belastningen från de talrika dikena och bäckarna samt de tre mindre åarna har ökat.

Estuarina miljöer är viktiga förökningsmiljöer för många fiskarter, men de är samtidigt ofta utsatta för syra- och metallbelastningen vid den Finska västkusten. Då variationerna i syra- och metallbelastningen sker snabbt är det svårt att förstå de totala konsekvenserna med endast sporadiska vattenprovtagningar. Den enkla metoden att mäta förekomsten av lakyngel (*Lota lota* L.) visade sig i Larsmo-Öjasjön ge jämförbara resultat i uppskattningen av syra- och metallbelastningen som täta vattenprovtagningar under flera månader. Den omfattande dataserien på vattenkvaliteten i Larsmo-Öjasjön bekräftar att ekologin i studieområdet är konstant hårt utsatt; förhållanden som kan ge försämrad lakyngelproduktion har inträffat nästan vart tredje år sedan 1975. De ofta återkommande mindre intensiva surchockerna, som uppenbarligen ändå kan orsaka störningar i produktionen av fiskyngel, har sannolikt större betydelse i fiskpopulationers utveckling än de relativt sällsynta stora surchockerna som orsakar synlig fiskdöd. Uppföljning av fiskyngelbestånd som bioindikatorer kan m.a.o. ge värdefull information om belastningens påverkan på vattenkvalitet och fiskstammar vid kustområden påverkade av sura sulfatjordar.

Fram till dags dato finns inga åtgärder för snabbt förbättrad vattenkvalitet i områden med sura sulfatjordar. Dirigering av utflödet från södra delen av Larsmo-Öjasjön för att rädda den norra delen är motiverat vid akuta surchocker, men det är noterbart att syra- och metallbelastningen endast leds om på detta sätt, och att metoden inte gynnar åarna eller havet utanför. Kalkning av vattendragen är mycket svårt p.g.a. de stora mängder kalk som skulle krävas. Reglering av grundvattennivån med hjälp av kontrollerad dränering i redan existerande sura sulfatjordar borde i teorin minska på belastningen, men det har varit oklart om metoden påverkar grundvattennivån/oxidationen i praktiken. Metoden testades tillsammans med en nergrävd plastfilm för att förhindra dräneringsvattnet från att rinna förbi

kontrollbrunnarna. Resultaten visade att metoden kan förhindra ökad belastning trots att dräneringssystemet blev mera effektivt för odlingsändamål. Det absolut säkraste sättet att minska på skadorna är att undvika dränering och torrläggning av sulfidsediment så långt som möjligt.

Konsekvent data är viktigt i studier av långtidstrender i vattenkvaliteten. Därför bör den nuvarande oregelbundna uppföljningen av vattenkvaliteten i många vattendrag uppdateras. Bioindikatorer visade sig vara viktiga i studierna av belastningen från sura sulfatjordar samt dess konsekvenser, speciellt då tillräcklig data på vattenkvalitet saknas. Bättre kunskap om belastningens beteende, inklusive i samband med en eventuell klimatförändring, efterföljande effekter på ekologin samt rätt utförda studier på miljömetoder kommer att hjälpa oss få förbättrad vattenkvalitet i framtiden.

List of publications

This thesis includes four papers, and Janne Toivonen was mainly responsible for the writing, data interpretation and most of the samplings and chemical analyses during the period 2007 – 2013. The papers are referred to with their Roman numerals in the text. Papers I and II are published by permission of the journals.

I. Toivonen, J., Österholm, P., 2011. Characterization of acid sulfate soils and assessing their impact on a humic boreal lake. Journal of Geochemical Exploration 110, 107 – 117.

II. Toivonen, J., Österholm, P., Fröjdö, S., 2013. Hydrological processes behind annual and decadal-scale variations in the water quality of runoff in Finnish catchments with acid sulfate soils. Journal of Hydrology 487 60 – 69.

III. Toivonen, J., Hudd, R., Fröjdö, S., Österholm, P., Short- and long-term variation in water quality and commensurable occurrence of burbot (*Lota lota* L.) larvae in a lake environment affected by acid sulfate soils. Submitted to Science of the Total Environment.

IV. Toivonen, J., Rosendahl, R., Yli-Halla, M., Österholm, P., Effects of controlled sub surface pipe-drainage on soil geochemistry in an acid sulfate soil. Manuscript.

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1. Introduction

1.1 Acid sulfate soils

Acid sulfate (a.s.) soils cause environmental problems worldwide in the form of high acidity and metal concentrations in water courses (Andriesse and van Meensvoort, 2006; Haraguchi, 2007; Hudd and Leskelä, 1998; Willet et al., 1993). Originally, these soils were created as a result of sediments deposited on the bottom of the sea together with large amounts of organic material. Conditions here were favorable for the microbial induced reduction of sulfate that was available in the sea water, and for the formation of sulfides, mainly in the form of pyrite (FeS_2) and metastable iron sulfide (ferrous monosulfides, FeS). In Finland sulfidic sediments were especially deposited in estuary environments during the Littorina and Postlittorina Sea stages of the Baltic Sea (7500 – 0 BP) when the coasts of Finland were submerged. A post-glacial land uplift rate of 8 mm per year in western Finland has placed them 0 – 100 m above sea level (normally below 40 – 60 m), resulting in the fact that today they underlie large parts of the river valleys and plains (Palko, 1994; Yli-Halla et al., 1999).

Although the Finnish sulfidic sediments may have been lifted high above sea level, they still mainly remain waterlogged due to the flat topography of the region, and are often covered by shallow lakes or peat. The sulfides are, thus, protected from coming into contact with air. However, these sediments are very productive soils if drained and limed. Consequently, whenever these sulfidic sediments are drained and come in contact with atmospheric oxygen they oxidize, and large quantities of sulfuric acid are produced, enhanced by microbial catalyzed oxidation (Wu et al., 2013). As a result, if the pH in the sediments drops below 4.0 due to sulfide oxidation, an acid sulfate (a.s.) soil is created. In this acidic environment, soil minerals start to dissolve, and potentially toxic metals (mainly Al, Cd, Co, Cu, Mn, Ni and Zn) in highly bio-available forms are released. These soils are flushed intensively during snow melt and heavy autumn rains due to the strong aggregate structure and artificial drainage, resulting in the discharge of very acidic and metal-rich water into streams (Åström and Björklund 1995; Österholm and Åström 2008; Palko and Yli-Halla 1988, 1990). In the 19th century, the peat lands in western Finland were drained by manually dug ditches and the peat was burned which exposed the sulfidic sediments to atmospheric oxygen. Many of the shallow lakes were also drained to gain new land. Some of the earliest fish kills related to acidic metal discharge were documented in the 19th century (Anonymous, 1896; Sutela et al., 2012; Suupohja, 1973). Later, the land use in the 1960s and 1970s was greatly intensified as a result of extensive drainage work and the installation of effective subsurface pipe-drainage. This caused the rate of sulfide oxidation to increase, resulting in a more or less permanent poor water quality and declining fish stocks in rivers and coastal areas in western Finland (Åström et al., 2005; Hildén and Rapport

1993; Hudd and Leskelä 1998; Paper II and III; Saarinen et al., 2010). Since then, high amounts of metals carried by the rivers have been deposited in estuaries, creating sediments with high concentrations of metals in easily soluble forms. These sediments may cause a renewed potential ecological risk if remobilized by dredging or re-suspension (Mcdonald et al., 2004; Nordmyr et al., 2008; Peltola and Åström, 2002).

When dealing with the toxicological effects on aquatic biota in acidic waters, Al is considered to be the most dangerous element (Poléo et al., 1997); it is also found to be the most abundant potential toxic metal released from a.s. soils (Fältmarsch et al., 2008; Österholm and Åström, 2004). The concentration and solubility of Al increases with decreasing pH (Nystrand et al., 2012; Poleo, 1995), and the toxic effect of Al on fish is mainly based on the accumulation of Al on the more alkaline gills, causing a disturbance of respiration and ion regulation (Gensemer and Playle, 1999; Poléo 1995). Aluminum concentrations in the range of 0.025 – 0.9 mg/l (measured as total-, filterable-, inorganic-, or labile monomeric form) have been shown to cause a disturbance and reduced survival in the eggs, juveniles and adult fish of various species. Although such results are even found in an almost neutral pH (pH 6.8; Hyne and Wilson, 1997), the toxicity of Al mainly occurs in the interval between 4.0 – 6.0 (McCahon et al., 1989; Rosseland et al., 1990; Sayer at al., 1993; Vuorinen et al., 1993; Waring and Brown, 1995). In addition to the high toxicity, the high concentrations of dissolved Al (and also Fe) cause extremely high acidity; the hydrolysis of metals may rapidly consume the buffering capacity in water courses. Therefore, compared to atmospheric deposition, another much discussed source of acidity, the draining of sulfidic sediments causes a build-up of total acidity corresponding to the accumulated acidity from thousands of years of acidic rain (Palko and Weppling, 1994).

Kills in adult fish are a well-known effect of acidic metal discharge. On the other hand, the full consequences are likely to be much more extensive than the relatively rare spectacular kills of adult fish. Estuaries offer important reproduction and nursing sites for coastal fish stocks in boreal environments due to the favorable temperatures and a high amount of available food and shelter found there. However, many estuaries in western Finland are susceptible to the discharge from a.s. soils carried by rivers (Lehtonen and Hudd, 1990). Moreover, the spawning and early life stages of fish are more sensitive to elevated acidity and Al. The frequent failure in the production of fish offspring, rather than the visible fish kills, has been suggested as the primary factor leading to declining fish stocks and fisheries in acidic environments (Hudd and Kjellman, 2002; Kjellman et al., 1994; Sammut et al., 1995; Sayer et al., 1993).

1.2 Study area

The Larsmo-Öja Lake (85 km^2, Fig. 1) is the largest embanked freshwater reservoir in Finland, and an estuary of four rivers; the Esse River (drainage area 2048 km^2, Photo 1), the Purmo River (866 km^2), the Kronoby River (767 km^2) and the Kovjoki River (292 km^2). The near-field (area drained by numerous low-order streams discharging directly into the lake) has a drainage area of 320 km^2, and the lake's total drainage area is 4290 km^2. The lake area was earlier a part of the inner archipelago of the Bothnian Bay with brackish water, but was embanked at narrow straits due to the industrial need for fresh water. The Larsmo Lake (73 km^2) was embanked in 1962 and the Öja Lake (12 km^2) in 1969, and a small canal links the two lakes together. The lake is an important spawning and nursing area for coastal fish species reproducing in estuaries, and constructed fish ways allow for the migration of fish between the lake and the sea. Due to recreational needs, the water level in the lake is kept stable at about 60 cm above normal sea level. Since the late 1960s, the lake has suffered from bad water quality and occasional fish kills due to low pH and high metal concentrations (Kalliolinna, 1996; Palko et al., 1987; Snickars and Wistbacka, 2000, Sutela et al., 2012). Because the lake is very important for industry, fishing and recreation, there is great local interest in the well-being of the lake. The latest fish kill that occurred in autumn and winter 2006 and 2007 is still a recent memory, and the reason for the reoccurring bad water quality has often been a subject of debate. As the fish kills did not occur before the embankments were built, the embankments have been blamed for the bad water quality. This is because the well-buffered brackish water is prevented to disperse into the lake to dilute and neutralize the acidic water. The reasons discussed as to the cause of the input of acidity to the lake in the first place have included atmospheric deposition, humic acids and dredging. The acid sulfate soils that are abundant in the coastal areas of western Finland are not always recognized in the discussions about the reasons for the bad water quality.

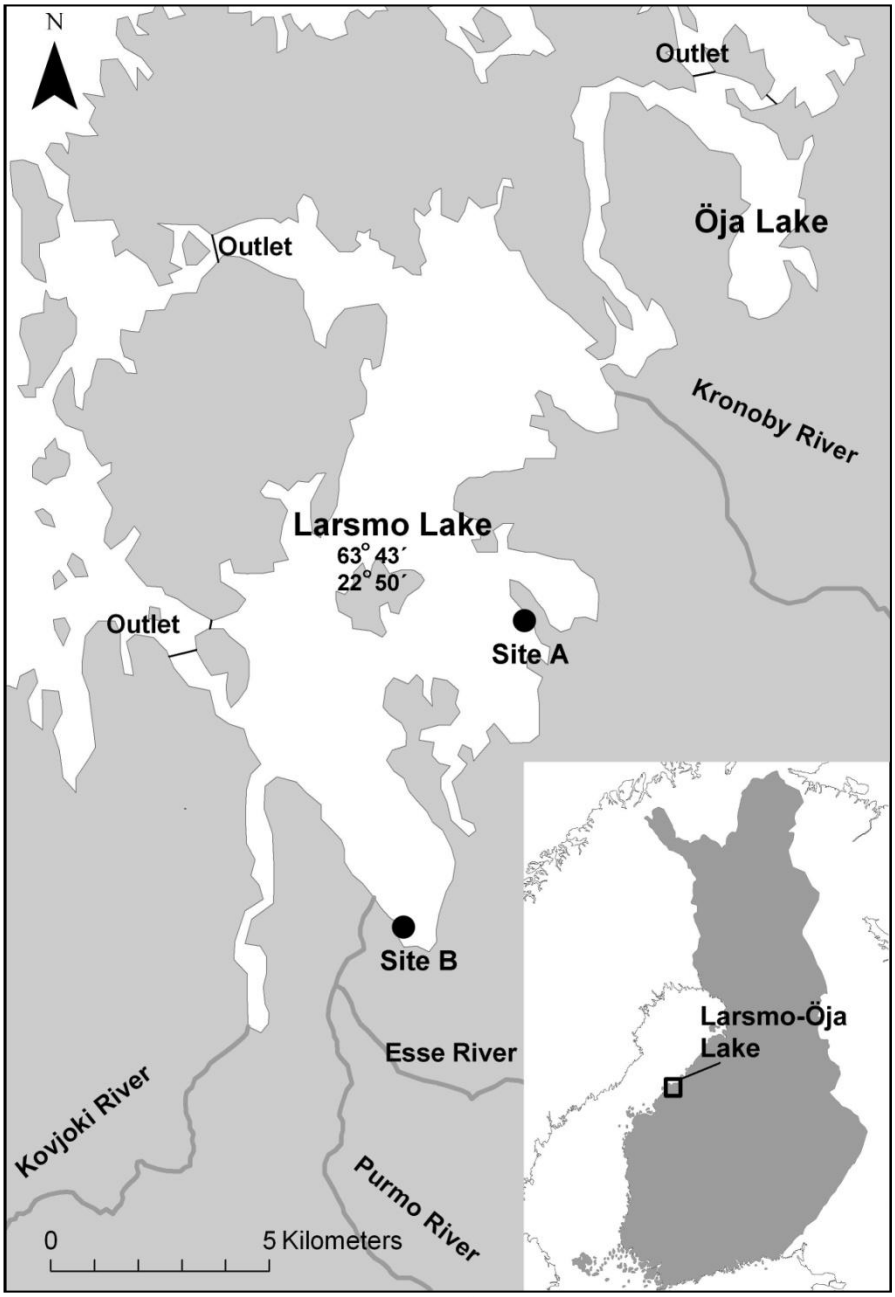

Fig. 1. Location of the studied Larsmo-Öja Lake system, rivers and the sites (A and B) for burbot larvae samplings.

Photo 1. The Esse River with the typical flat river valley where the probability of finding a.s. soils and sulfidic sediments is high.

1.3 Aims of the research

Four different papers are included in this work, and the six main aims are: 1) to quantify the different sources of the acidity (Paper I); 2) to study the behavior of the acidic metal load in the area in relation to land use and different meteorological conditions, and based on this discuss the consequences of a potential climate change (Paper II and III); 3) to study the interaction between river discharge and lake water quality (Paper III); 4) to study the impact of the acidity on coastal fish stocks and the potential use of bio indicators (Paper III); 5) to study and discuss possible mitigation methods (Paper I, II and IV); and 6) to elaborate upon laboratory methods for sulfur speciation in acid sulfate soils (Paper IV and unpublished data). Previous studies have only focused on rivers, and to a lesser extent on estuaries. This study provides a unique view on the behavior of acidic metal discharge in a lake system and the subsequent ecological impact. The best chances of improving water quality and ecological status are provided as a result of having better knowledge on the origin, behavior and environmental effects of acidic metal load and the effects of different mitigation methods.

2. Materials and methods

An overview of the materials and analyses is presented in Table 1, and in more detail in Paper I and IV. Some previously unpublished material is also included.

Table 1. Overview of the materials, methods and parameters used for soil- and water samples in Papers I – IV. Only elements and methods presented in this thesis are shown here.

Paper	Media	Area	Database	Year/period	n samples	Parameters	Methods
I	Soil	Soil in the catchment of Larsmo-Öja Lake (10 profiles)		2008	242	pH	Electrode
					35	S, Al, Cd, Co, Cu, Fe, La, Mn, Ni, Ti, V, Zn	Aqua regia, ICP/MS & ES
					25	Total acidity	Titratable peroxide acidity
					9	Grain size	Hydrometer
	Water	Low-order streams		April 2007	29	pH	Electrode
					29	EC	Electrode
					29	SO_4^{2-}	SFS-EN ISO/IEC 17025:2005
					29	Acidity	potentiometric titration to pH 8.3 within 24 h
					29	TOC (Total organic carbon)	Shimadzu Total Organic Carbon analyzer
					28	$\delta^{34}S$	Isotopic measurments (ICP-MS)
					8	Metals: Al, Cd, Co, Cr, Mn, Ni, Zn	0.45 µm, ICP/MS & ES
		Larsmo-Öja Lake		April 2007	11	pH, EC, SO_4^{2-}, acidity, $\delta^{34}S$, TOC, metals	Defined above
				August 2007	7	pH, EC, SO_4^{2-}, acidity, TOC, metals	"
				November 2007	9	"	"
				December 2007	4	"	"
		Esse-, Purmo-, Kronoby- and Kovjoki Rivers		April 2007	4	pH, EC, SO_4^{2-}, acidity, TOC, $\delta^{34}S$	"
				August 2007	4	pH, EC, SO_4^{2-}, acidity, TOC	"
				November 2007	4	"	"
				December 2007	4	"	"
		Esse River, five sites 2 – 25 km from the outlet		December 2007	5	pH, EC, SO_4^{2-}, acidity, metals	"
		Lestijoki	HERTTA	2007		Specific runoff, L:s/km^2	Measuring station
II	Water	Esse-, Purmo-, Kronoby- and Kovjoki rivers		December 2007	4	pH, Acidity	Defined above
		Esse River	Jakobstad Water Plant	1963 – 2009		pH	"
				1969 – 2009		Temperature, C^0	Thermometer
				1985 – 2009		Total Al	ICP-ES on unfilered samples
				1987 – 2009		EC	Defined above
		Pahkaoja stream	HERTTA	1963 – 2012		Specific runoff, L:s/km^2	Measuring weir
III	Water	Larsmo Lake	UPM-Kymmene Paper Mill	1975 – 2012		pH, EC	Defined above
						SO_4^{2-}	SFS 5738 and SFS-EN ISO 10304-1
						Total Al	SFS 5736 1992
				2005 – 2012	29 – 186/year	Occurrence of burbot larvae	One lite plastic scoop
IV	Soil	Soil in the catchment of Larsmo-Oja Lake (6 profiles)		2009 – 2013	204	pH	Defined above
					12	AVS and CCRS	"
					66	Actual acidity	"
Thesis	Soil	Soil and sediments in western and southern Finland		2010	46	AVS and CCRS	Diffusion based sulfur speciation
					18	Total S	Aqua regia and Eschka´s fusion
		Dredge spoils excavated from Larsmo Lake		2009	13	pH	Defined above
					10	Total acidity	"
					10	Actual acidity	KCl-extractable titratable acidity
	Water	Esse River	Herrfors hydro-power plant	2000 – 2009		Specific runoff, L:s/km^2	Measuring station

2.1 Sediments

2.1.1 Acid sulfate soils

Ten soil profiles were sampled with an auger in 2008 to characterize possible a.s. soils according to modern standards. Because only flat, low-lying and large farmlands (such as in Photo 1) were sampled, where the possibilities of finding sulfidic or sulfuric materials were high, the results do not describe the relative abundance or area of a.s. soils. The following horizons were identified: an upper plow layer rich in organic matter (Ap horizon), an oxidized horizon (pH<4, if found), a transition horizon (pH 4.2 – 6.5) and a reduced horizon (pH>6.5).

2.1.2 Dredge spoils

The calculation of the theoretical acidic load entering Larsmo-Öja Lake from dredge spoils was based on the maximum average amount of sediments excavated per year, which have been about 16,000 m^3/year in later years. The sulfur concentration in potential dredge spoils was estimated to be 0.5 – 0.7% (Åström and Björklund, 1997; Peltola and Åström, 2002). The bulk density of dredge spoils was estimated to be 1000 kg/m^3. The calculation of the acidic load is based on the overall reaction of the oxidation of pyrite (FeS_2) and metastable iron sulfide (FeS), and the precipitation of Fe(III) oxyhydroxide. These reactions produce one mole of sulfuric acid for each mole of sulfur. The simplified reaction of pyrite is shown below:

$$FeS_{2(s)} + 3.75O_{2(g)} + 3.5H_2O_{(aq)} \rightarrow 2SO_4^{2-}{}_{(aq)} + Fe(OH)_{3(s)} + 4H^+{}_{(aq)}$$

To gain some understanding of the potential acidity and leaching rate of acidity from dredge spoils in the study area samples were taken in autumn 2009 at a location in the western Larsmo Lake from freshly dug dredge spoils excavated during the previous winter (winter 2008 – 2009). Additional samples were taken from dredge spoils that had been oxidized and leached on dry land in a roughly 60 cm thick wall for ten years (Toivonen, unpublished results).

2.1.3 Sulfur species

Since land use that cause the oxidation of sulfides may lead to extreme acidic soils and the consequent deterioration of the ecology in nearby water courses, information about the abundance and distribution of different sulfur species, together with the total sulfur content, is useful for evaluating the environmental impact from land use. Also, the effects of mitigation methods that enable sulfidization may be evaluated by this method. Metastable iron

sulfide and pyrite are the main sulfides found in sulfidic sediments and the content is dependent on the reagents and procedures used in the analysis. Metastable iron sulfide is considered to mainly consist of mackinawite ($FeS_{1.0}$) and greigite ($FeS_{1.34}$, Boman et al., 2008) and give the sediments a characteristic black color. Pyrite (FeS_2) is more stable, while the black metastable iron sulfides oxidize very rapidly upon contact with atmospheric oxygen. Consequently, excavated sediments rich in metastable iron sulfides will oxidize and lose their characteristic black color within hours (Boman et al., 2010).

In order to describe the content and distribution of different sulfur species, mainly sulfides that have the potential to cause environmental problems (metastable iron sulfides and pyrite) sulfur speciation was performed on soil samples from the study area. At the same time, the suitability of the diffusion method in Finnish circumstances was tested by performing sulfur speciation on samples from an additional three areas in Finland (Toivonen, unpublished results; Toivonen and Virtanen, unpublished results). The main method used for determining sulfur species has been the purge-and-trap method (Backlund et al., 2005), where a continuous N^2 flow carries the H_2S for later analysis. However, this is a relatively expensive and time-consuming method to determine sulfur in large number of samples. In view of this, a diffusion-based method has been developed by Burton et al. (2008), Hsieh and Shieh (1997), Hsieh and Yang (1989) and Ulrich et al. (1997), where the reactions take place in a closed chamber, and a large number of samples can be analyzed simultaneously. The metastable iron sulfides are defined as acid-volatile sulfur (AVS) and pyrite as Cr(II)-reducible sulfur (CRS).

Analysis of the AVS and CRS fractions with the diffusion method was performed on samples from six profiles taken from the reduced horizon (250 – 280 cm depth) of an agricultural field (same field as in section 2.4) in the catchment of Larsmo-Öja Lake. Sulfur speciation was also performed on samples taken from locations where sulfur speciation with the purge-and-trap method has been performed in earlier studies: one sample from the reduced sediment (280 cm depth) of an agricultural field in Korsholm (earlier sulfur speciation performed in Boman et al., 2008), and one sample from about one-meter-depth from reduced peat covered sediments in the Bay of Vassor (earlier sulfur speciation performed in Boman et al., 2010, site G). The determination of AVS, CRS and total sulfur was also performed on several samples taken from the poldered cultivated a.s. soil of the University of Helsinki at Viikki in southern Finland, and on samples from the experimental monoliths (described in Virtanen et al. (2013)).

The samples used in this study were taken with an auger or Russian sampler and immediately frozen in dry ice to minimize oxidation. For the determination of sulfur species, a sample was cut from the frozen sample, and any oxidized surface material was scraped off. 300 – 600 mg of soil (dry equivalent) was weighed into a 50 ml reaction flask. A subsample was

weighed for determination of dry weight. A small tube containing 7 ml alkaline zinc solution (4% Zn acetate) was inserted in the reaction chamber. For the extraction of AVS, 10 ml of 6 M HCl and 2 ml of 1 M ascorbic acid were added into the reaction chamber in an anoxic environment. After an 18 – 24 hour reaction time on a shaking board (150 rpm), the small tube with precipitated Zn sulfide was removed, and the sulfur was quantified via iodometric titration.

For the determination of CRS a 2 M Cr solution was made by dissolving chromium(III)chloride hexahydrate ($CrCl_3*6H_2O$; purity 98%) in 10.4 M HCl. Metallic Zn was added under anoxic conditions (constant purging with N_2) to allow the Cr(III) to reduce to Cr(II), which was indicated by a color change from dark green to dark blue. A new tube with a fresh alkaline Zn solution was added to the reaction chamber, and about 12 ml of the acidic Cr(II) solution was added to the reaction chamber under an anoxic environment. The reaction was allowed to take place during 36 hours on a shaking board, after which the trapped Zn sulfide was quantified via iodometric titration. Since the recovery of CRS was low compared to the total sulfur in some samples, the HCl and ascorbic acid solution used in the extraction of AVS were removed in some of the analyses by centrifugation before the addition of acidic Cr(II) solution to prevent dilution. A direct one-step CRS procedure, without first removing the AVS fraction, can also be performed to determine the total reducible sulfur (TRS, sum of AVS and CRS (Hsieh and Shieh, 1997)).

The total sulfur concentrations in some samples were determined by aqua regia extraction. Some additional analysis of total sulfur with Eschka's fusion (two parts magnesium oxide and one part sodium carbonate) was also performed: about 3 g of Eschka's mixture per one gram of oven dry sediment was weighed in a porcelain crucible with an additional layer of Eschka's mixture on top. The sample was heated to 800 ^{0}C for two hours for the sulfur to oxidize to sulfate. The fusion residue was transferred to a 500 ml Erlenmeyer flask and dissolved in 200 ml deionized water. After simmering for 30 minutes, the solution was filtered and pH was adjusted to less than 4. Excess (10 ml) $BaCl_2$ was added dropwise while stirring and the solution was left overnight at 60 ^{0}C before filtering, drying and weighing the precipitated $BaSO_4$ (Backlund et al., 2005; Tuttle et al., 1986).

2.2 Water

Electric conductivity (EC) is dependent on the amount of ions in the water. In contrast to most coastal areas worldwide, the tides are negligible in the Gulf of Bothnia, and there is no significant intrusion of brackish water into streams, rivers or lakes in western Finland. Therefore, in areas in Finland with significant occurrences of a.s. soils, ions leached from these soils dominate EC in water courses. This is seen in the strong correlations between

EC and a.s. soil-related elements (Åström and Åström, 1997; Österholm and Åström, 2008; Paper I and II; Roos and Åström, 2005a). Due to differences in the soil characteristics (grain size and sulfur content) and land use (drainage depth) the variations in EC can be site-specific, i.e. the relationship between EC, pH and a.s. soil-related elements varies between different catchments. Consequently, together with pH, data on the relative variance in EC in these water courses can be used as an indicator on impact from a.s. soils. In addition, pH and EC are easily measured and the methods have not changed through time. Therefore, long-term data on pH and EC are reliable and different data sets are comparable.

Non-parametric statistical methods were mainly used in this study because most geochemical data sets show skewed distributions and outliers (Reimann and Filzmoser, 1999). Also, 10^{th} percentiles, medians and 90^{th} percentiles were mainly used because they are robust against outliers and errors (Helsel and Hirsch, 2002).

Because different fish species, life stages and populations show different sensitivities to low pH and high Al concentrations, and speciation of Al plays a significant role in toxicity (Nystrand, 2012; Poleo, 1995), it is difficult to establish an exact threshold value with harmful pH and Al concentrations. However, Al is considered most toxic in pH below 5.5 (Witters, 1998), and pH below 5.5 and below 5.0 has also been adopted in the national classification system as the threshold values to moderate and poor water quality, respectively (Vuori et al., 2009). Therefore, pH below 5.5 and below 5.0 was used in this work to indicate very acidic and extremely acidic water quality, respectively.

Because the analysis of Al in the long-term data sets used in Paper II and III was performed on unfiltered samples, the Al concentrations may partly originate from erosion, or occur in particulate form (Nystrand et al., 2012). However, results from studies in a.s. soil-affected areas in western Finland (Åström and Björklund, 1995; Nystrand and Österholm, 2013) and in the current study area (Roos and Åström, 2005a; Papers I – III), together with the flat topography (Photo 1) and the lack of the characteristic clay colored water typical of erosion, indicates strongly that erosion is not a major contributor to Al concentrations. Therefore the total Al concentrations in the available data are regarded to mainly reflect discharge from a.s. soils.

Although analysis of water filtered through a 0.45 µm filter is commonly used to obtain the dissolved and potentially toxic fraction of the metal concentrations, according to recent studies, a substantial amount of the "dissolved" metals occur, in fact, attached to colloids. The colloidal metals tend to be less toxic than truly dissolved metals, and the conventional filtering through a 0.45 µm filter may therefore lead to an overestimation of the toxicity (Nystrand et al., 2012; Nystrand and Österholm, 2013). In this work, the term "dissolved" is, however, still used for metal concentrations that pass through a 0.45 µm filter.

An overview of the sampling, analysis and methods concerning water follows below and in Table 1. More detailed information is found in Papers I – III. Some additional unpublished material is also included.

2.2.1 Characterization and quantification of the acidic metal load on Larsmo-Öja Lake

In order to understand the origin, character and quantity of the acidic metal load, sampling and flow estimation of the low-order streams, rivers and lake was performed during different hydrological conditions in 2007 and 2008. High concentrations of sulfate (indicator of sulfuric acid), Al, Cd, Ni and Zn are good indicators on the impact from a.s. soils, and the quantities discharging into Larsmo-Öja Lake were calculated as a runoff-weighted average according to Bydén et al. (2003). Long-term data sets on water quality in the Esse River and Larsmo Lake were obtained from Jakobstad water plant and UPM-Kymmene paper mill in Jakobstad. These data were used to describe the long-term water quality, and 10^{th} percentiles, medians and 90^{th} percentiles were mainly used. Since the data on the lake represent water quality in the southern part of the lake system, only Larsmo Lake will be discussed unless otherwise mentioned. Long-term data on specific runoff were obtained from the nearby unregulated Lestijoki River and Pahkaoja stream.

Besides the standard potentiometric titration to pH 8.3, acidity according to pH 5.5 as the end point was analyzed in order to estimate the neutralization demand (ND) and limestone requirement in the rivers during the late autumn 2007. pH 5.5 as an end point was used because it corresponds to a minimum desired pH at a liming procedure (Palko and Yli.-Halla, 1993), and because most of the toxicity of Al is removed at this pH (Witters, 1998). Since powdered limestone is the main agent used in liming procedures, the poor dissolution of limestone in acidic and metal rich waters cause the ND often to be twice as high compared to the results from titrations using e.g. NaOH (Weppling, 1993). Calculations of ND was based on the entire river water discharge into Larsmo-Öja Lake during the 2000s during the time when pH in the Esse River dropped below 5.5, because it is then when the situation in Larsmo-Öja Lake becomes very critical. Runoff data from the unregulated Pahkaoja stream was used to calculate the flow for the three smaller rivers. Since the Esse River is regulated upstream at the large Lappajärvi Lake, separate runoff data were used for the Esse River using the actual flow measured at Herrfors hydropower plant that is located close to Larsmo-Öja Lake.

2.2.2 Effects of hydrology on water quality

The average specific runoff was highest in May (24 L s^{-1} km^{-2}) and November (11 L s^{-1} km^{-2}) for the spring and autumn seasons, respectively, and the pH was generally low in these months (table 4). February and July showed the lowest average specific runoff (1.9 and 2.3 L s^{-1} km^{-2}, respectively) and generally high pH. Based on this, data from the 15th of February, May, July and November were chosen to represent changes in water quality related to runoff in both the Esse River and Larsmo Lake during the four seasons, and non-parametric Lowess smoothing (f=0.67) was used.

The effect of dry summers was studied by correlating (Spearman rank correlation, p=0.05) the average runoff during the summer against the 10th percentile and median pH, and the median and 90th percentile EC during the following autumn and spring. For autumns, additional correlations were performed on data where days with low and moderate runoff (runoff<10 L s^{-1} km^{-2}) were excluded from the calculations of pH and EC.

2.2.3 Interaction between river discharge and lake water quality

The vulnerability of Larsmo-Öja Lake was estimated by performing mixing tests during two periods of high runoff in November and December 2007. Water from the four rivers discharging into the lake was mixed in proportion to their catchment size. The pH was measured in the combined river water, and slowly titrated to different samples from the lake until pH decreased to less than 5.5. The lake retention time was calculated by dividing the lake volume (200 million m^3) with the total discharge (m^3/s) the sampled day. Changes in the water quality in Larsmo Lake in relation to changes in the Esse River were studied by correlating (Spearman rank correlation, p=0.05) pH and EC the fifteenth of every month and medians the previous 5, 10 and 30 days in the Esse River with data on pH and EC from the fifteenth of every month in Larsmo Lake.

To investigate the dispersion of the river water in the lake, water samples were taken in the discharging rivers and low-order streams during a period of high runoff in the spring 2007, and in the lake about one week later. The samples were analyzed for isotopic ratios of sulfur (S^{34}/S^{32}) reported as $\delta^{34}S$. At the time of sampling, only the southern outlet to the sea was open.

2.2.4 Long-term trends

Because pH and EC are robust parameters in estimating impact from a.s. soils (see Section 2.2), they are the main parameters used for trend analysis in this work. The long-term data sets obtained from Jakobstad water plant (Esse River) and UPM-Kymmene paper mill (Larsmo Lake) were used in the trend

testing. Data from the fifteenth of every month were the most widely used in the trend testing unless otherwise mentioned, and enables the use of runoff-corrected pH and EC (Hirsch et al., 1991). The non-parametric Kendall's tau and seasonal Kendall's trend tests were used, and the level of confidence was set to 95% (p=0.05). Additional tests were performed on the 10^{th} percentile and median pH, and the median and 90^{th} percentile EC for every month. Additional data on specific runoff, temperature, total Al and sulfate concentrations were also used for trend testing. The additional data on the water quality obtained from the HERTTA database (OIVA-environment and geographic information service, Finnish Environment Institute) were too irregularly sampled and inconsistent in the choice of analyzed parameters to provide any valid results from trend analysis, and the data were only used to give an approximate trend.

In addition, rather than observing measured pH, trends in water quality were detected by considering the frequency of acidic events of two degrees; here defined as the number of times when pH is below 5.5 or 5.0 for at least one day during the month in question. The data were divided into ten-year periods to observe trends in the frequencies.

2.3 Effects of a.s. soils on the occurrence of burbot larvae

An overview of the material is presented in Table 1, and in more detail in Paper III.

The production of burbot (*Lota lota* L.) offspring is especially vulnerable in areas with a.s. soils because both the timing and habitat preferences of spawning, egg-, and juvenile stages are susceptible to the acidic metal discharge (Hudd and Kjellman, 2002; Lehtonen and Hudd, 1990; Rask et al., 1995). Burbot larvae were sampled in order to study the possible connection between the acidic metal discharge and production of burbot offspring in optimal habitats at two locations in Larsmo Lake 2005 – 2012 with 2010 missing at site A; and 2005 and 2010 missing at site B (Fig. 1). Potential larval areas in the study area were mapped and modeled by Hudd et al. (2007), and the only variable explaining the occurrence of burbot larvae was the availability of shallow water with floating dead common reed (*Phragmites australis)*. The samplings for this study were performed during the first half of May each year in optimal habitats, and the probability of capturing any larvae per sample was used as an index of abundance and expressed as the hit rate. The critical period for reproduction success of burbot used in this study begins with the spawning peak (set at February twenty-fifth, Hudd, 2000) and ends when the last larvae samplings were performed (May fifteenth). pH statistics (minimum and 10^{th}, 25^{th} percentile and median pH) during this period in the Esse River and Larsmo Lake was correlated against the hit rate (Spearman rank correlation, p=0.05). To more

precisely detect the transient periods crucial for the abundance of larvae, the studied period was not only divided into shorter intervals (5, 10, 20, 30 and 40 days) for which pH statistics were calculated, but also extended to the autumn before the sampling, since the migration of burbot into spawning areas begins in late autumn. The pH-statistics that were correlated (Spearman rank correlation, $p=0.05$) against the hit rate included 10^{th} percentile pH, median pH and amount of days with pH below a number of different threshold values.

2.4 Enhanced controlling of the ground water level

An overview of the material is presented in Table 1, and in more detail in Paper IV.

Managing a.s. soils and sulfidic sediment in order to prevent environmental damage should be based on preventive measures (i.e. avoiding draining and oxidation of sulfidic materials). The installation of effective subsurface pipe-drainage has shown to significantly increase environmental impact from a.s. soils compared to the traditional shallow open drains (Palko and Yli-Halla, 1993). However, since the a.s. soils in Finland are of great value due to their high yield, there is great interest in finding techniques to reduce environmental impact, while, at the same time, enable continuous intensive use. Controlled subsurface pipe-drainage (CPD) is a technique where the drainage depth can be regulated in wells at the end of the main drain pipes. This enables an effective drainage system during spring, and the theoretical possibility to prevent significant drops in the ground water level during the summer and, consequently, decrease the risk of sulfide oxidation during the growing season. Even though the effects are poorly studied, the technique has already been widely installed in many a.s. soils in Finland. Moreover, the few existing short-term studies have so far shown that CPD has not provided the desired effects on ground water level or soil- or water geochemistry compared to conventional pipe-drains. This is mainly due to a combination of factors, including deep soil cracks and macropores that allow any discharge to pass by the drainage system, strong evapotranspiration causing low ground water, and/or poor management (Österholm et al., 2012). The installation of CPD is therefore likely to cause similar enhanced environmental effects as the installation of conventional subsurface pipe-drains unless the technique and management plans are improved.

The effect of CPD on soil acidity was studied in a rather ineffectively drained but deeply oxidized field underlain by silt in the catchment of Larsmo-Öja Lake. Vertical plastic sheets were installed at a depth of 30 – 180 cm around the whole field in order to prevent by-pass flow and overall lateral seepage, and to force all discharge through the regulated wells. The field contained three subfields with one well each. Two of the sub-fields were

forested previous to the installation of CPD, while the third sub-field was already in agricultural use but drained with shallow (about 70 cm) open drains. Two soil profiles per subfield were sampled and analyzed for soil acidity before the installation of CPD in 2009, and after the installation in 2010 and 2013. This was done in order to detect possible changes in soil acidity induced by the installation of the effective drainage system.

3. Results

3.1 Sediments

3.1.1 Soil

Measurements of soil pH showed that seven of the ten soil profiles sampled from different farmlands in the lake catchment had a sulfuric horizon (showing pH less than 4.0 within 150 cm of the mineral soil surface, and had sulfidic materials underneath), or had sulfidic materials under a histic horizon (found within 100 cm of the soil surface, Paper I), therefore meeting the criteria for Sulfic Cryaquepts or Sulfisaprists (Soil Survey Staff, 2010), respectively. Incubation of soil samples from the remaining three profiles decreased pH by a minimum of 0.5 units to less than 4.0 (indicating sulfidic materials), therefore also meeting the criteria for a Sulfic Cryaquept. The depth where the reduced horizon begins (where pH>6.5), and an indicator of the minimum ground water level, varied between 130 and 240 cm (median 200 cm). The total sulfur concentrations in the sulfuric and sulfidic materials were high (0.13 – 1.6%) and the concentrations correlated significantly with titratable peroxide acidity (total acidity, Fig. 2). The sulfuric and/or sulfidic material was in some profiles relatively thin (<200 cm), and there was overall great variation in the sulfur concentration, acidity and grain size within profiles and between profiles. Excellent correlations between the clay fraction (<0.002 mm) and Fe, La, V, Cd, Ti, Cu, Zn, Ni, Mn, Al and Co (r_s=0.92 – 1.0) were found

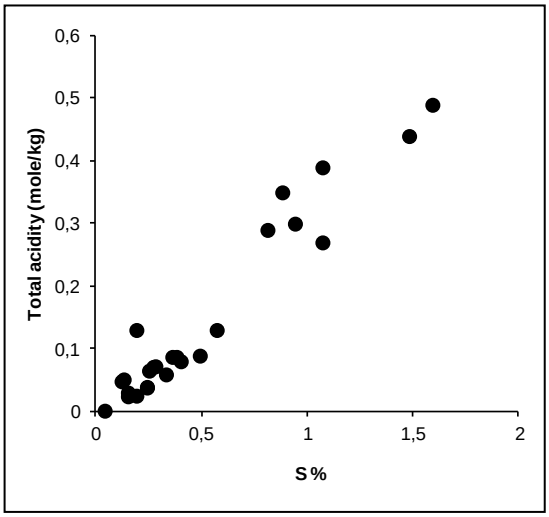

Fig. 2. Total sulfur versus total acidity in the mineral soil (r_s=0.90).

3.1.2 Dredge spoils

Analysis of the fresh dredge spoils showed that the material had oxidized during the summer, but there was great variation in pH (2.5 – 6.4) which was a result of the different sampling depths and resulting difference in the oxidation state. The total acidity was 0.09 – 0.28 (median 0.14) mole/kg. The samples that had a pH below 4.0 was analyzed for KCl-extractable acidity (actual acidity), which was 0.06 – 0.15 (median 0.07) mole/kg. Analysis of the ten-year old dredge spoils in the same area showed a pH of 4.4 – 4.5 at a depth of 20 – 60 cm and 4.1 in the upper 20 cm. The total- and actual acidities were 0.0 – 0.02 mole/kg in the whole profile. The result from the estimated acidic load from the amount of dredge spoils excavated each year in the Larsmo-Öja Lake is presented in Section 3.2.2, and discussed in Section 4.2.1.

3.1.3 Sulfur speciation

The samples from the oxidized horizon (120 – 150 cm) from six profiles from a location close to the Larsmo Lake showed that median AVS was 0.05% (0.01 – 0.08%), median CRS was 0.26% (0.0 – 0.34%) and the sum of AVS and CRS was 0.27% (0.05 – 0.39%, Table 2, Paper IV). The results for the reduced horizon (250 – 280 cm) were median AVS: 0.08% (0.02 – 0.14%), median CRS: 0.25% (0.07 – 0.83%), and the sum of AVS and CRS: 0.32% (0.21 – 0.90%).

Table 2. Acid volatile sulfur (AVS), Cr(II)-reducible sulfur (CRS) and total sulfur based on aqua regia (AqR) in soil samples from western Finland (Larsmo-Öja, Vassor and Korsholm) and southern Finland (Viikki).

	AVS			CRS			AqR			Comments
	Min	Med	Max	Min	Med	Max	Min	Med	Max	
Larsmo-Öja Oxidized horizon n=6	0.01	0.05	0.08	0.0	0.26	0.34				Sulfur speciation performed on samples from six different profiles
Larsmo-Öja Reduced horizon n=6	0.02	0.08	0.14	0.07	0.25	0.83				
Vassor reduced horizon n=6	0.47	0.49	0.56	0.18	0.25	0.35				Sulfur speciation performed on duplicate samples
Korsholm reduced horizon n=11	0.14	0.17	0.37							Sulfur speciation performed on duplicate samples
n=2				0.10	0.12	0.13				
n=2 *				0.25	0.26	0.26				
Viikki Reduced horizon n=13	0.0	0.0	0.02	0.07	0.73	1.8	1.5	1.7	2.2	Sulfur speciation performed on samples from thirteen different profiles

*Samples where the HCl and ascorbic acid solution was removed after the AVS procedure in order to improve the recovery of CRS.

The tests to obtain the suitability of the diffusion method in Finnish sulfidic materials continued with sulfur speciation performed on samples from three other locations in Finland: The results from six duplicates taken from one single sample from a location at Vassor Bay showed median AVS: 0.49% (0.47 – 0.56%, Table 2). Median CRS was 0.25% (0.18 – 0.35%) and the sum of AVS and CRS was 0.76% (0.67 – 0.82%).

The results from the second location (Korsholm) showed median AVS 0.14% (0.10 – 0.37%) and median CRS 0.10 (0.10 – 0.13%). The median AVS and CRS fractions were low compared to an earlier study (0.36 and 0.19%, respectively, Boman et al., 2008), and there was a negative correlation between the sample weight and AVS concentration (r_s=-0.86). Some further small-scale testing on well homogenized duplicate samples indicated that increasing the reaction time for the AVS procedure from 24 to 48 hours during the AVS procedure increased the recovery (Table 2 shows

the combined results from the two AVS-procedures, n=11). An attempt to improve the recovery of pyrite by removing the HCl and ascorbic acid solution from the reaction chamber by centrifugation after the AVS had been extracted led to a significant increase in the median CRS content from 0.12 to 0.26%.

Speciation performed on the samples from the third a.s. soil-location (a.s. soil and experimental monoliths from Viikki) showed practically no AVS (median 0%), while the median CRS was 0.73% (0.07 – 1.8%) and the median aqua regia sulfur was 1.7% (1.5 – 2.2%, Table 2) in the reduced horizon. The low TRS (AVS + CRS) compared to aqua regia sulfur gave a suspicion of incomplete recovery of the CRS, and prompted further testing. Further analysis was performed on a sample from one of the experiment monoliths from the reduced horizon. The sample was homogenized thoroughly. New determinations of AVS, CRS, total sulfur with Eschka´s mixture and aqua regia, and also TRS based on the one-step CRS procedure, were performed. The results were compared with the previous determinations (Table 3). Since a removal of the HCl and ascorbic acid solution after the AVS-procedure proved to increase the recovery of CRS in the Korsholm samples, this method was tested. The previous sulfur determination on the sample resulted in median AVS: 0%, CRS: 0.73%, aqua regia sulfur: 1.5% and TRS: 3.2%. The new determination gave 0.03% (0.02 – 0.03%) AVS. Duplicate samples analyzed with the conventional CRS method showed slightly lower concentrations (1.6 and 1.7%) than the duplicates where the HCl and ascorbic acid were removed before the CRS determination (1.8%). The total sulfur content based on analysis with aqua regia performed on a single sample showed 1.9%, and the duplicates analyzed with Eschka's mixture both resulted in 2.1%. The TRS (performed as a one-step CRS procedure) performed on duplicate samples resulted in a sulfur content as high as 2.8 and 3.1%.

Table 3. Determination of AVS, CRS, total sulfur (aqua regia, AqR and Eschka´s fusion) and one-step CRS (TRS) on one sample from Viikki in southern Finland

Previous determination	**AVS**	**CRS**	**AqR**	**TRS**	
	0	0.73	1.5	3.2	
New determinations performed on homogenized samples	**AVS** n=4	**CRS** n=2	**AqR** n=1	**Eschka** n=2	**TRS** n=2
	0.03 (0.02 – 0.03)	1.6 (1.6 – 1.7) n=2* 1.8 (1.8 – 1.8)	1.9	2.1 (2.1 – 2.1)	3.0 (2,8 – 3.1)

*Samples where the HCl and ascorbic acid solution was removed after the AVS procedure for an attempt to improve the recovery of CRS.

3.2 Water

3.2.1 General water quality in streams and rivers discharging into Larsmo-Öja Lake

Electric conductivity (EC) and concentrations of sulfate and many metals typical of discharge from a.s. soils (Cd, Mn, Zn, Al, Ni and Co) in the studied low-order streams were very high and pH was very low: 11 – 141 times higher and 1.2 units lower, respectively, compared to the medians in 1161 headwater streams in Finland (Lahermo and Väänänen, 1996; Paper I). The concentrations were, however, somewhat lower compared to medians in western Finland found by Åström and Björklund (1995), except for Zn and EC that were similar, and pH and sulfate were somewhat higher. There were significant correlations between sulfate and a number of a.s. soil-related parameters, such as pH, EC, acidity and Al (Fig. 3, Paper I), in the low-order streams. Significant negative correlations were found between total organic carbon (TOC) and acidity (Fig. 4) and a positive correlation between TOC and pH (r_s=0.77, Paper I).

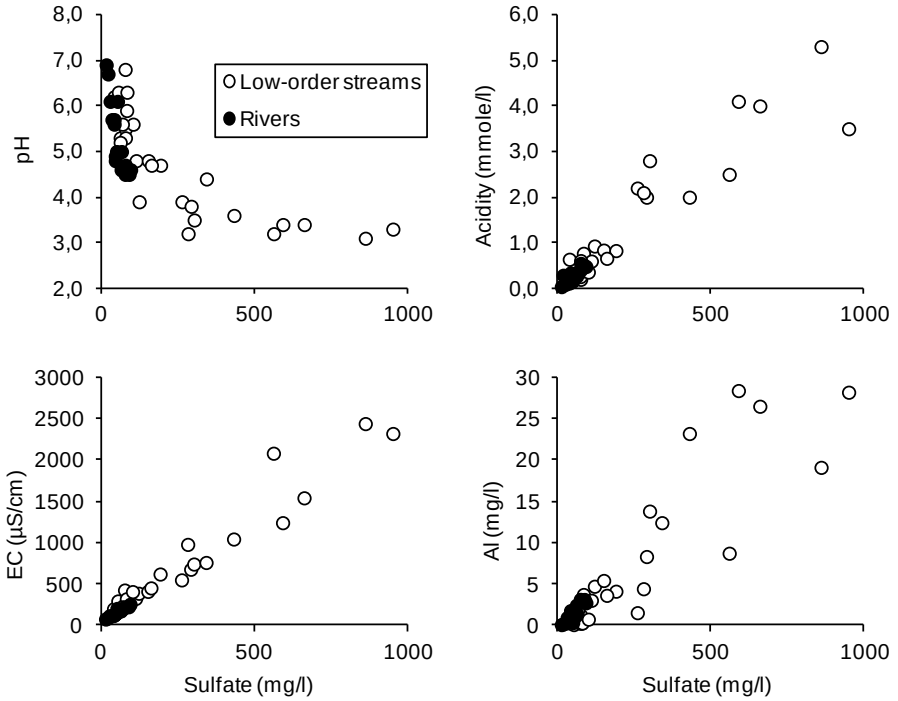

Fig. 3. Sulfate versus pH (r_s for the streams/rivers: -0.88/-0.85), acidity (0.89/0.78), EC (0.95/0.98) and Al (0.89/0.88).

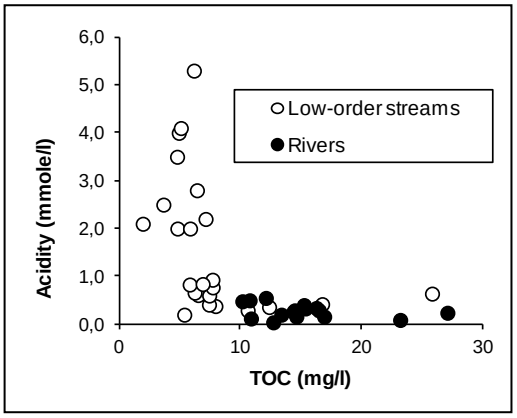

Fig. 4. Total organic carbon (TOC) versus acidity in the low-order streams (r_s= -0.67) and rivers (not significant).

Electric conductivity as well as concentrations of sulfate and most of the same characteristic metals for a.s. soils were also clearly elevated in all of the four rivers discharging into Larsmo-Öja Lake. The most affected river, Kovjoki River, showed EC and concentrations of Al, Cd, Co, Mn, Ni and Zn that were 2.5 – 23 times higher compared to Lappfjärd River, one of the few rivers in the area that is relatively unaffected by a.s. soils. In the four studied rivers, there were also significant correlations between sulfate and a number of a.s. soil-related parameters (pH, acidity, EC and Al (Fig. 3, Paper I). Paper II and Paper III showed that the Esse River and the recipient Larsmo Lake have both experienced pH below 5.5 in about nine years out of ten since 1975. Extremely acidic circumstances (pH<5.0) have occurred more often in the river, six out of ten years, compared to about five out of ten years in the lake. Even though extreme pH may be more common in the river, Larsmo Lake was overall more acidic and metal rich (Table 4, Fig. 7, 8 and 9). In general, the month of May showed the lowest pH during a year in the Esse River, while both May and December showed the lowest pH in the lake (Table 4). The months with the highest EC in the river were October – December and April – May, and October – January in the lake. The medians of total Al concentrations in the Esse River were highest in April – June (0.11 – 0.40 mg/) and October – December (0.10 – 0.53 mg/l). No data on sulfate were available for the Esse River. Larsmo Lake showed the highest medians of total Al in April – May (0.55 – 0.64 mg/l) and in October – January (0.40 – 0.69 mg/l), while highest medians of sulfate concentrations were found in May and June (29 – 30 mg/l) and November – February (30 – 39 mg/l). Data on total Al and sulfate are not shown.

Table 4. 10th percentile and median pH, and median and 90th percentile EC in the Esse River and the Larsmo Lake during different months (1975 – 2009 for pH and 1989 – 2009 for EC).

	Esse River				Larsmo Lake			
	pH		EC (mS/m)		pH		EC (mS/m)	
	10 percentile	Median	Median	90 percentile	10 percentile	Median	Median	90 percentile
Jan	6.0	6.4	7.4	10	5.5	6.0	13	16
Feb	6.1	6.4	7.5	8.6	5.8	6.1	12	15
Mar	6.1	6.4	7.5	9.3	5.8	6.2	12	14
Apr	5.4	6.1	8.1	11	5.3	6.0	11	15
Maj	5.0	6.1	7.5	11	5.2	5.9	11	15
Jun	5.9	6.6	7.2	8.9	5.5	6.1	12	15
Jul	6.3	6.7	7.0	8.4	5.9	6.3	12	16
Aug	6.2	6.7	6.9	8.8	6.0	6.4	12	16
Sep	6.1	6.7	7.0	8.6	5.9	6.5	12	15
Okt	5.6	6.5	8.0	11	5.6	6.4	12	15
Nov	5.4	6.4	8.6	13	5.4	6.0	13	17
Dec	5.7	6.4	8.1	12	5.2	5.9	14	18

Based on the sampling during high runoff in December 2007 at five sites, the spatial trend in the Esse River showed stable pH, EC, acidity, sulfate and metal concentrations at the first three sites (50 – 20 m above sea level, Fig. 5, Paper I). Downstream from there, a 0.9 unit drop in pH and a 1.6 – 4.5 -time increase in EC, acidity and sulfate-, Al-, Ni-, Zn- and Cd concentrations occurred at the last sampling point before discharging into the lake.

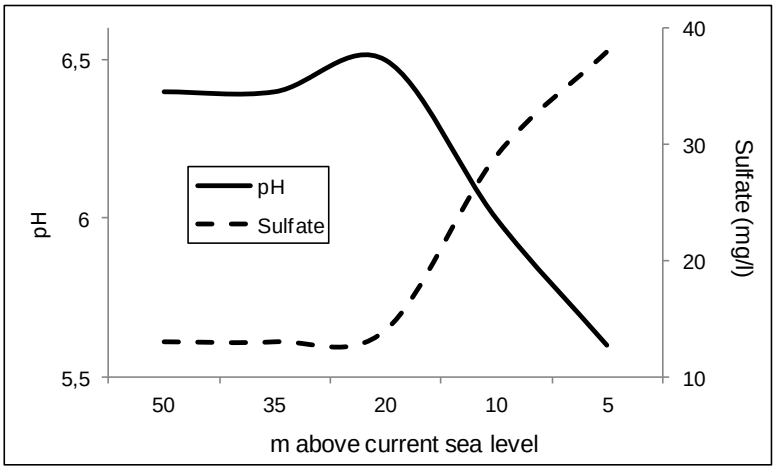

Fig. 5. Spatial changes in pH and sulfate in the Esse River.

3.2.2 Quantification of the acidic metal load on Larsmo-Öja Lake

The discharge of sulfuric acid during one year to Larsmo-Öja Lake was in the order of 65,000 t. Of this load, the Esse River contributed by 30%, the Purmo River by 22%, the Kronoby River by 16%, the Kovjoki River by 10% and the low-order streams in the near-field by 23% (Paper I, Fig. 6). Same calculations performed on the concentrations of some a.s. soil-related metals show that Larsmo-Öja Lake received roughly 2,300 t of Al, 60 t of Zn, 20 t of Ni and 0.2 t of Cd in dissolved form (0.45 µm), of which 34, 28, 31 and 32%, respectively, originated from the low-order streams in the near-field (Fig. 6, Toivonen and Österholm, unpublished data). Calculation of the acidic load from the dredge spoils excavated each year showed that the amount of sulfur would be 80 – 112 t, leading to 245 – 340 t of sulfuric acid when oxidized. This is only 0.38 – 0.52% of the total load carried to the lake.

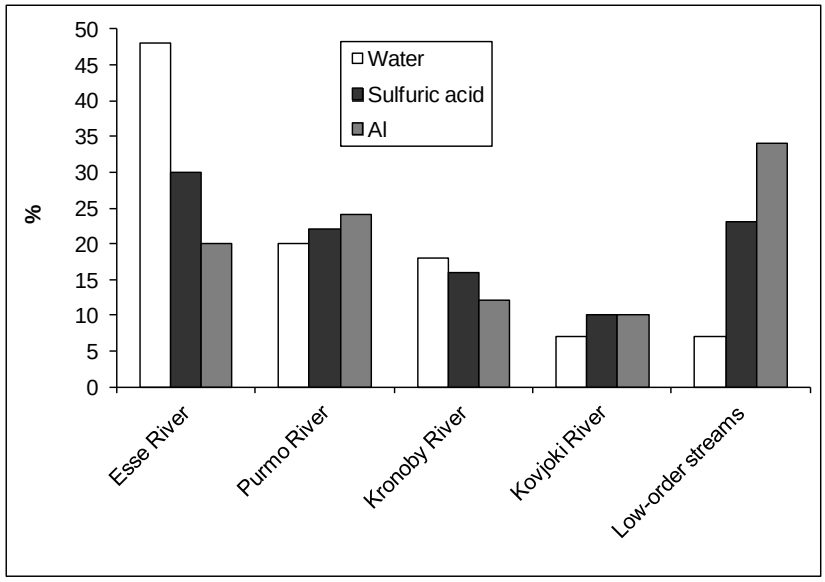

Fig. 6. Share (%) of total water-, sulfuric acid- and Al discharge to Larsmo-Öja Lake from the rivers and low-order streams.

The neutralization demand (ND), expressed as the amount of limestone needed to raise pH to 5.5, during an autumn period with a specific runoff of about 15 L s^{-1} km^{-2} showed that 26 t/day was needed in the Esse River (field-pH 5.2 and 8.8 g $CaCO_3/m^3$). When all four rivers were sampled a few days later, the pH in the Esse River was above 5.5, and not analyzed for ND. Total limestone requirement in the three smaller rivers was 32 t/day; the Kovjoki River (field-pH 4.6) needed 22 g/m^3, the Purmo River (field-pH 4.5) 16 g/m^3, and the Kronoby River (field-pH 5.0) 4.8 g/m^3 (Paper II). These ND-values

have been multiplied with two to counteract the poor dissolution rate of limestone. The calculation of the ND during each year was based on the assumption that the ND in all rivers are as presented above. The pH in the Esse River did not drop below 5.5 during three years (2002, 2005 and 2008), and the ND was therefore not calculated for these years. During the remaining seven years, the ND would have been 340 – 3300 t limestone/year (average 1400 t) to neutralize all river water discharging to Larsmo-Öja Lake. This amount was spread on the 3 – 46 days/year (average 17 days/year) when the Esse River showed pH below 5.5, and the daily dosage would therefore have been 50 – 220 t (average 100 t).

3.2.3 Effects of hydrology on water quality

Serious declines in pH often occur rapidly with increasing runoff in water courses affected by a.s. soils as seen in the great variation in runoff and corresponding changes in pH (Fig. 7 and 8, Paper II and III). In general, very small or no changes at all in pH or EC was visible in February and July (Fig. 7, 8 and 9). In May and November, the lowest pH in both the Esse River and the Larsmo Lake was found at runoff>10 – 20 L s^{-1} km^{-2}, but dilution during May prevented a linear drop in pH (Fig. 8). Electric conductivity acted similarly in both the river and the lake; an initial increase in November was visible up to about 10 – 20 L s^{-1} km^{-2}, while no clear trend in EC with increasing runoff was visible during the other seasons.

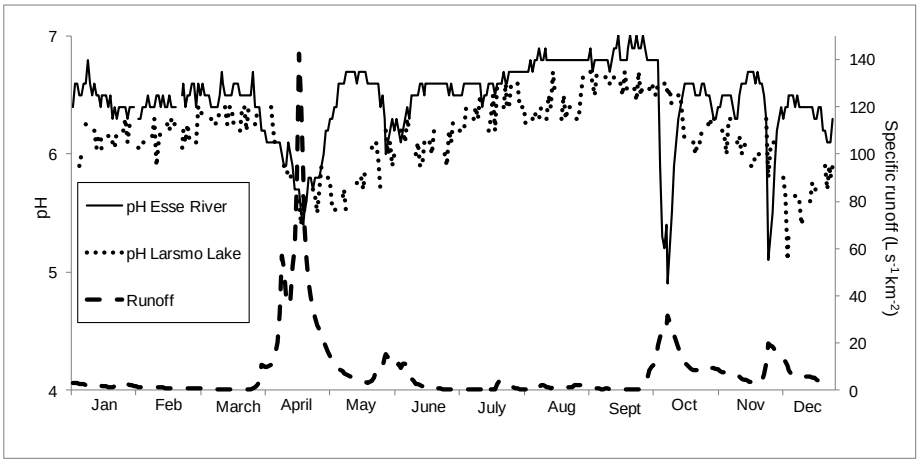

Fig. 7. Water pH in the Esse River and the Larsmo Lake and specific runoff from the nearby Pahkaoja stream during 1999.

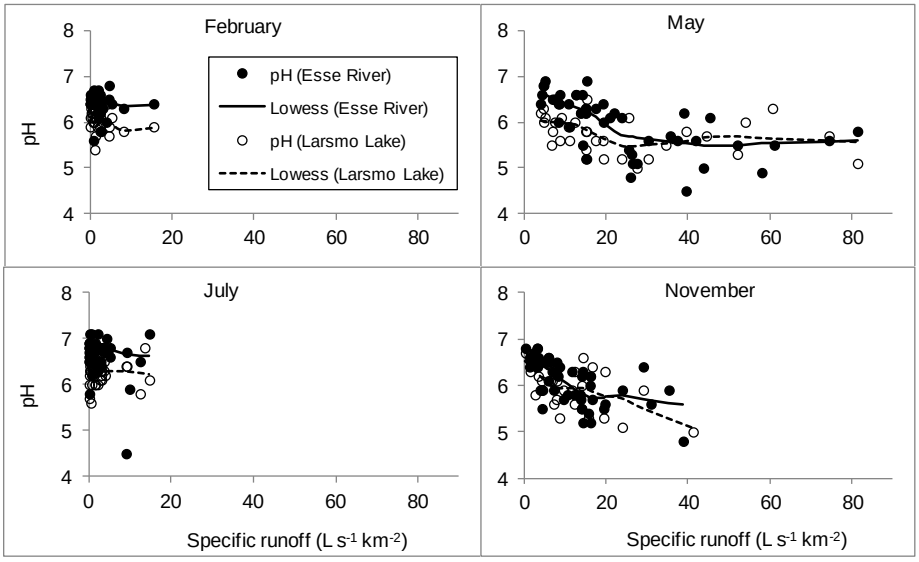

Fig. 8. Potential relationship between specific runoff and pH in the Esse River and the Larsmo Lake indicated by the Lowess curve.

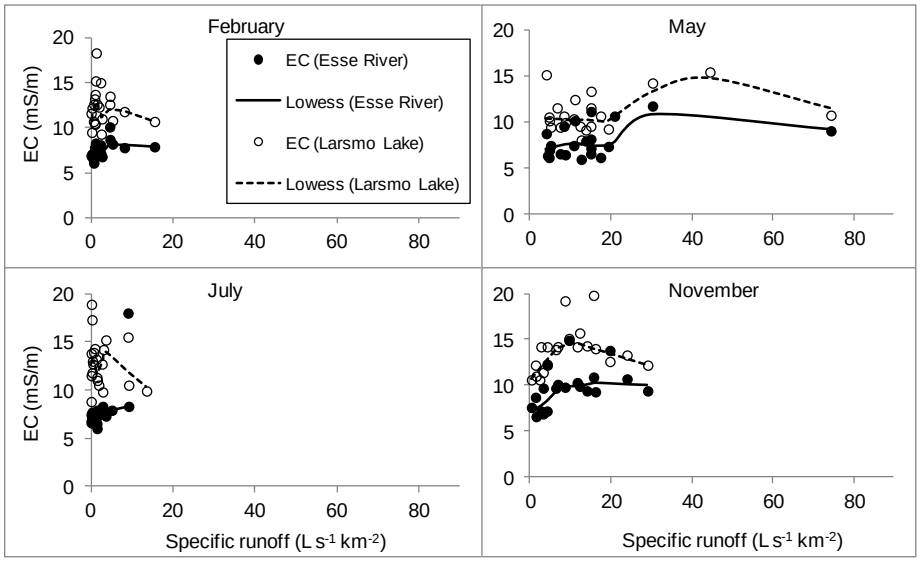

Fig. 9. Potential relationship between specific runoff and EC in the Esse River and the Larsmo Lake indicated by the Lowess curve.

The average runoff during the summer did not seem to have an obvious effect on the water quality following autumn (measured as a 10^{th} percentile and median pH, and median and 90^{th} percentile EC) in the Esse River or Larsmo

Lake (Paper II and III). Instead, specific runoff during the autumn seemed to be more decisive in controlling pH (average specific runoff vs. median pH showed r_s=-0.64 for the Esse River and r_s=-0.60 for Larsmo Lake). Since high runoff is crucial for water quality, autumn days with low runoff (runoff<10 L s^{-1} km^{-2}) were excluded from the calculations of the pH- and EC statistics during the autumn, and the correlation between summer-runoff and water quality the following autumn became significant (r_s=0.48 for 10th percentile pH and r_s=0.55 for median pH, and r_s=-0.65 for median EC and r_s=-0.64 for 90th percentile EC) for the Esse River, but not for the Larsmo Lake. In contrast, a direct correlation was found between average summer-runoff and 10th percentile and median pH during the following spring in the river (r_s=0.49 and 0.37, respectively) and the lake (r_s=0.49 and 0.40, respectively), but not EC.

3.2.4 Interaction between river discharge and estuary water quality

The combined river water that contained water from the four rivers in proportion to their catchment size had a pH of 5.0 at both sampling events in November and December (Paper III). The lake water samples used had a pH between 5.9 and 6.5, and about 50 – 67% of the river water was needed to lower pH to less than 5.5. During both samplings, specific runoff was about 20 L s^{-1} km^{-2}, and the theoretical lake retention time was therefore about 27 days.

There was no impact from pH in the Esse River on Larsmo Lake during the months characterized by low runoff (January, February, July and August, Paper III). During the other months, as expected, the river affected pH in the lake, but mainly with a delay since the most significant correlations were found when using 10- and 30 day median pH in the river. Only April showed a slightly better correlation when using a one- or 5 day median pH. No link between EC in the river and the lake was found during June – October. During the other months, mainly one- and 5 day medians in the Esse River correlated with EC in the Larsmo Lake.

The $\delta^{34}S$ values, indicating the dispersion pattern of water in the lake, were -5.4 – -6.1 in the three bigger rivers, and -4.4 – -6.2 in the southern and middle part of the lake. The values were slightly more positive in the northern part (-2.6 – -4.3, Paper I).

3.2.5 Long-term trends

A temporal trend showing a decline in pH occurred in both the Esse River (Paper II) and Larsmo Lake (Paper III) in the late 1960s and early 1970s. After the worst period in the early 1970s, the pH has continuously recovered in the Esse River until today (Seasonal Kendall: tau=0.23). The incoherent data on Larsmo Lake acquired from the HERTTA database would indicate a

recovery during the winter and summer already in the mid-1970s, and until the 1990s during the spring and autumn. In contrast to the increasing pH in the Esse River and the seemingly increasing pH in the lake, the vast and continuous data on Larsmo Lake starting from 1975 does not show such an improvement. The runoff-corrected pH also shows a weak but significant increasing trend (tau= 0.08) for the Esse River, but not for the Larsmo Lake. However, the frequency of acidic events seemed to be highest in the 1980s in the lake except for the cold season, which, in turn, showed an increased frequency of acidic events in the 2000s, both in the river and the lake (Fig. 10, Paper III).

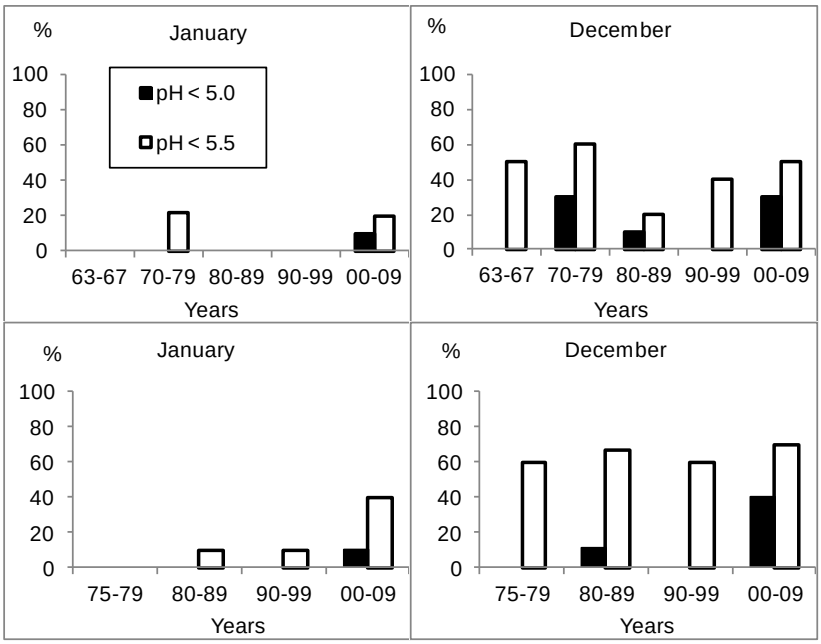

Fig. 10. Months (%) when pH has decreased for at least one day to less than 5.5 and 5.0 in January and December during different decades in the Esse River (upper graphs) and the Larsmo Lake (lower graphs).

Electric conductivity has increased in the Esse River since 1987 (tau= 0.35). However, no trend in EC is found for Larsmo Lake except for the months of January (tau=0.53), August (tau=-0.40) and October (tau=-0.36). The trend in total Al since 1985 has decreased in the Esse River (tau= -0.09) but increased in Larsmo Lake since 1975 (tau= 0.38 and 0.36 since 1985). Sulfate concentrations in the lake showed no trend since 1989, except for the month of January (tau=0.43). Because the sulfate analysis method changed in 2004 the observed trend is somewhat uncertain.

3.3 Effects of a.s. soils on the occurrence of burbot larvae

In spring 2006, the hit rate (chance to find at least one burbot larvae per scoop) was as high as 62% at site A, which coincides with the highest median pH in both the Esse River and Larsmo Lake (Fig. 11, Paper III). However, an extreme acidic event occurred in autumn 2006 and continued in spring 2007, causing the lowest median pH and an absence of burbot larvae in 2007. Also 2012 showed low pH and an absence of burbot larvae, but in contrast to the situation in 2007, no visible fish kills were reported. Even though several different pH-statistics (minimum and 10^{th} and 25^{th} percentile pH) were tested for correlations, only the median pH seemed to affect the hit rate. The correlation between the pH in the Esse River and the hit rate at site A is significant, but not when using the pH in the Larsmo Lake. No clear connection between pH and hit rate was found for site B, but the two extreme years of 2006 and 2007, regarding pH and hit rate, are also very prominent (figure not shown).

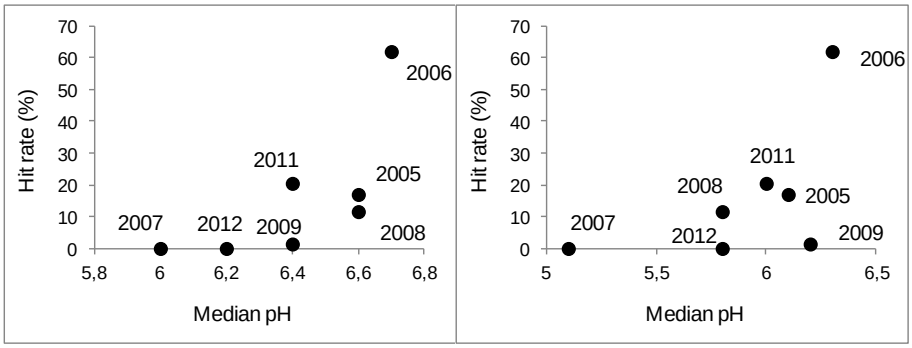

Fig. 11. Link between median pH during the critical time of reproduction (February twenty-fifth to May fifteenth) in the Esse River (left, r_s=0.83) and the Larsmo Lake (right, not significant) at site A.

When using the more detailed periods, the pH-statistics during a period beginning in late November to late December in the Esse River correlated significantly with the hit rate at site A (Paper III). A second period with similar results occurred from late February to late March. In addition to the 10^{th} percentile and median pH, the number of days with pH<6.4 – 6.5 seemed to indicate a threshold value. The same results were found for the lake, but the critical periods occurred from late December to early February, and from late March to mid April, and the number of days with pH<5.9 – 6.1 seemed to be most crucial.

3.4 Enhanced controlling of the ground water level

The soil profiles that were sampled during the four-year test period (2009 – 2013) had high total sulfur concentrations (up to 1.5%) and showed low minimum pH values (3.2 – 4.1, Paper IV). The soil was classified as a Sulfic Cryaquept (Soil Survey Staff, 2010) due to the sulfuric horizon (pH<4) found within 150 cm of the soil surface. Root canals coated with iron precipitates (pipe stems) down to 250 cm and the jarosite ($KFe^{3+}_3(OH)_6(SO_4)_2$) occurrences are typical in a.s. soils. A fairly low AVS content was found in the reduced (250 – 280 cm) samples (Table 2), which was also evident by the relatively light color. The CRS content was generally higher in the profiles. The median oxidation depth, indicated by the depth where pH<6.5, was 230 – 240 cm both previous and after the installation of CPD. The pH was low and actual acidity was high already previous to the installation, and showed no major change during the four years after installation of CPD other than increased pH in the plow layer (upper 20 cm, Fig. 12).

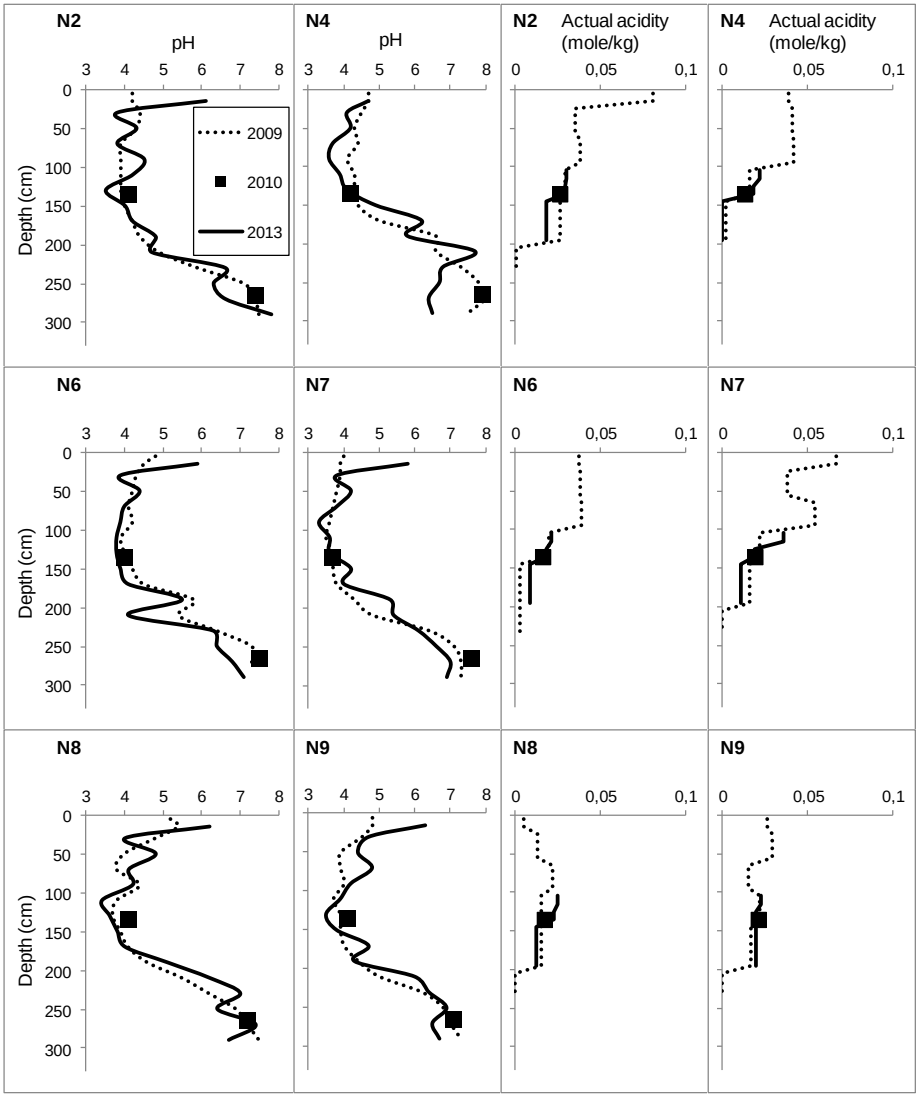

Fig. 12. Soil pH (two columns on the left) and titratable KCl-exchangeable actual acidity (end-point pH 5.5, two columns on the right) in the six profiles 2009, 2010 and 2013.

4. Discussion

4.1 Sediments

4.1.1 Soil

All of the ten profiles in the catchment of the study area fulfill the criteria of a.s. soils according to modern standards (Soil Survey Staff, 2010). They contain a great pool of acidity, having a potentially profound harmful effect on the water quality and biota in the recipient water courses. The excellent correlation between clay content and concentrations of many elements shows that the variation in soil metal concentrations is largely controlled by grain size; easily weathered phyllosilicates dominating the clay fraction are the main source of metals (Österholm and Åström, 2002). The great variation in grain size, sulfur- and metal concentrations within profiles, as well as between profiles, indicates that the a.s. soils in the catchment of Larsmo-Öja Lake are very heterogeneous and generally coarser and shallower compared to other a.s. soils in western Finland studied by Åström (1998), Nordmyr et al. (2006) and Österholm and Åström (2002). The shallowness of the sulfuric horizon or sulfidic materials in some profiles (indicated by S%<0.13) may cause some reservations in the determination of the oxidation depth; the rise in pH at a certain depth may be related to low sulfur concentrations rather than due to anoxic conditions. The occurrence of a.s. soils in the study area is confirmed by the recent release of a probability map of the occurrence of a.s. soils based on a mapping project by the Geological Survey of Finland and Åbo Akademi University (Geological Survey of Finland, 2013a).

4.1.2 Dredge Spoils

The analysis of pH and acidity content in fresh dredge spoils in a location in western Larsmo Lake showed that the sediments at the bottom of the lake will oxidize and become a.s. soils (pH down to 2.5) and release large amounts of acidity if excavated and put on dry land. The theoretical neutralization demand (TND) based on the total acidity was 4.4 – 14 kg $CaCO_3/m^3$ to neutralize all potential acidity to pH 5.5. However, the actual lime dose required may prove to be significantly higher due to incomplete dissolution of the limestone (Palko and Weppling, 1994). Analysis of the dredge spoils that have been oxidized and leached for ten years showed that the main pool of acidity in these sediments has the potential to leach, and the material will consequently become relict a.s. soils, within ten years. This was indicated by pH>4 and TND$\leq$1.0 kg $CaCO_3/m^3$ in dredge spoils excavated ten years previously. The leaching within ten years is considerably faster than what is reported for a.s. soils on farmlands, where the estimated half-time of the rate of sulfur leaching is roughly 30 years, but the harmful leaching of

acidity and metals may continue for a significantly longer period (Österholm and Åström, 2004). The rate of leaching in the analyzed dredge spoils may have been enhanced by a coarse grain size and enhanced oxidation circumstances; dredge spoils are often put on dry land and spread out in shallow layers or piles resulting in more effective oxidation compared to a.s. soils that are drained by ditches or pipe-drains. Therefore, dredge spoils that are not properly managed (put too close to water and/or not limed) may have a more severe effect on water quality in the short-run than the same amount of a.s. soils created by draining operations.

4.1.3 Sulfur speciation

The results from the sulfur speciation performed on the samples from Vassor Bay (TRS, the sum of AVS and CRS, was 0.67 – 0.82%) appeared to give comparable results with an earlier speciation performed with the purge and trap method, where TRS was up to 0.88% (Boman et al., 2010). This gave an indication of a decent recovery of the different sulfide species with the diffusion based sulfur speciation.

A low AVS content was evident in most of the samples taken from the reduced horizon in the catchment of Larsmo-Öja Lake by a generally lighter color. Only a few of the samples showed an AVS content above 0.10%, which was recognizable in the field by a black color of the sediments. However, analyses of total sulfur concentrations (aqua regia and Eschka´s fusion), showed that the TRS fraction only made up roughly 50% of the total sulfur. This indicates a poor recovery since the TRS content in reduced sediments should be more than 90% (Boman et al., 2008, 2010). The results from the Korsholm sample would also indicate a poor recovery of both AVS and CRS compared to the results found by Boman et al. (2008), but prolonging the reaction time of AVS, and the removal of the HCl and ascorbic acid solution after the AVS step seemed to improve the recovery.

The AVS fraction in the samples from Viikki in southern Finland was practically zero, which was also indicated by the absence of any characteristic black coloring. The CRS determination also indicated a poor recovery compared to aqua regia sulfur, when the TRS made up less than half of the aqua regia sulfur in reduced sediments. Some further small-scale testing on duplicates indicated that the sulfur concentrations can vary significantly within just centimeters when the new determination of CRS and total sulfur (aqua regia) taken from the same frozen samples resulted in clearly different results, and duplicates on subsamples that were thoroughly homogenized showed reasonably good accuracy. Further results were that the one-step CRS determination resulted in a much higher TRS content compared to the TRS calculated as the sum of AVS and CRS (even though CRS recovery was improved by removing the HCl after the AVS procedure). Also, total sulfur analysis performed with Eschka's mixture resulted in higher

concentrations than those analyzed after digestion with aqua regia (but not as high as the TRS performed with the one-step CRS determination). The new analysis of aqua regia sulfur that was performed on the homogenized sample showed, however, that the TRS (AVS+CRS) was about 90% of the total sulfur, which would indicate reasonable recovery (Boman et al., 2008, 2010). However, since the analysis performed with Eschka's mixture still showed higher total sulfur content, and since aqua regia is known to be unable to recover some sulfides, the total S content according to Eschka's mixture seems more reliable.

For the study of the sulfur species in the catchment of Larsmo-Öja Lake, the diffusion based method proved to be qualitatively sufficient; the dominating sulfur species was pyrite with lesser content of reactive monosulfide. However, different physical, chemical and mineralogical settings in the soil between areas probably cause difficulties in the determination of more exact quantities. Also, the sulfur content in the soil may vary significantly within just a few centimeters. This highlights the importance of homogenizing the sample before analysis, especially if parallel analyses on duplicates with different methods are performed. A prolonged reaction time for AVS (48 hours instead of 24) and removal of the HCl and ascorbic acid solution before the CRS determination seemed to improve the recovery. Further testing to improve overall recovery could be performed with some kind of stirring of the sample inside the reaction chamber. There was also often great difference between the determinations of total sulfur (aqua regia and Eschka's mixture), and between AVS+CRS and TRS (one-step CRS). It is important to note that the diffusion based sulfur speciation is operationally defined, and the results indicate that the method needs improvement and more complete testing to be applicable on the sulfidic and sulfuric materials in boreal environments.

4.2 Water

4.2.1 Water quality and quantification of the acidic metal load

A total of 21 rivers in mid-western Finland were ranked by Roos and Åström (2005b) according to concentrations of potentially toxic metals caused by discharge from a.s. soils. The rivers discharging into Larsmo-Öja Lake were placed close to the median (the Kovjoki River) or contained relatively low concentrations of potentially toxic metals (the Purmo-, Kronoby- and Esse Rivers). Despite the relatively low input of discharge from a.s. soils compared to many other rivers in mid-western Finland, the geochemical pattern between pH, acidity, sulfate- and metal concentrations in the four rivers discharging into Larsmo-Öja Lake strongly indicate a significant influence from a.s. soils. The discharge from a.s. soils is by far the most important cause of low pH and high metal concentrations in the study area.

Peat lands and coniferous forests are a source of organic carbon (OC) in boreal environments, which contain a large part of organic acids, and the organic acids normally control pH in water courses (Laudon et al., 1999; Mattson et al., 2007). However, the low-order streams and rivers discharging into the Larsmo-Öja Lake showed an opposite pattern between OC and pH. Consequently, the acidic load that OC contributes is insignificant compared to the load from a.s. soils (Mattsson et al., 2007). Instead, OC is known to buffer and decrease some of the harmful effects in heavily acidified and metal rich water courses (Vuorinen et al., 1999; Witters et al., 1990).

The long-term data shows that pH has dropped and metal concentrations have increased in all four rivers and the lake to harmful levels more or less on a regular basis, which explains the poor ecological and chemical status found by Vuori et al. (2009). The spatial trend related to impact from a.s. soils in the Esse River during a period of normal high runoff in autumn 2007 showed that the water quality is stable with little input from a.s. soils≥20 m above current sea level. This is confirmed by more long-term data from the HERTTA database; pH has rarely decreased below 6.0 at sampling points≥20 m above sea level. Acid sulfate soils do, in fact, occur in areas≥20 m above current sea level in the catchment of the Esse River (Geological Survey of Finland, 2013b), but the proportion of a.s. soils is too small for any significant deterioration in water quality. As the river flows closer to the coast, there is a dramatic input of discharge water from a.s. soils indicated by a lowered pH and increased acidity, sulfate- and metal concentrations. The spatial pattern of declining water quality toward the coast as the proportion of a.s. soils in the catchment increase can be found in many rivers in western Finland (Åström, 2001; Åström and Spiro, 2005; Edén et al., 1999; Nystrand et al., 2012; Nystrand and Österholm, 2013; Roos and Åström, 2005a). The relatively more acidic and metal-rich three smaller rivers discharging into Larsmo-Öja Lake frequently show signs of decline in water quality due to acidic metal discharge already at 40 – 60 m above current sea level (about 25 – 40 km from the coast; Beucher, pers. comm.; HERTTA database; Känsälä and Björkgård, 2002). The relative difference in water quality in the four studied rivers is a result of different distribution of a.s. soils in the catchments (Palko and Yli-Halla, 1993); the discharge waters from a.s. soils are most diluted in the Esse River because a large part of the catchment lies above the highest coastline of the Littorina Sea stage. The catchments of the three smaller rivers reach above the Littorina Sea coastline to a lesser extent, and the low-order streams draining the near-field have catchments exclusively below the highest coastline of the Littorina Sea stage. Correspondingly, even though the low-order streams in the near-field only drain 7% of the catchment of Larsmo-Öja Lake, they contributed during 2007 with as much as one fourth of the total sulfuric acid load, which was only surpassed by the large Esse River (accounts for almost 50% of the catchment of Larsmo-Öja Lake), and equal to Purmo River. The metal load from the low-order streams

was as high as about one third of the total load, and the share was larger than from any of the rivers. The relatively lower load of metals, comparing to sulfuric acid from the rivers to the low-order streams, may be because the metals are transported a larger distance in the rivers, and come in contact with more complexing agents, such as OC, and well-buffered ground water which promotes removal of the metals from the water body by precipitation, complexiation and sedimentation. Sulfate, which is an indicator of sulfide oxidation and the amount of produced sulfuric acid, is a conservative ion and is not as easily removed from the water by geochemical processes.

The estimated maximum amount of dredge spoils excavated each year in Larsmo-Öja Lake is 16,000 m^3, and the theoretical amount of sulfuric acid produced from this amount of dread spoils is insignificant compared to the load carried by the streams and rivers. The load equals the amount the Esse River carries to the lake in only 24 hours during a normal high-runoff period in the autumn. Yearly excavations of about 40,000 m^3 of dredge spoils would be needed to reach 1% of the total load on the lake, and close to 0.5 million m^3 to reach 10%. Peltola and Åström (2002) presented results from laboratory tests, where sediment samples from the bottom of Larsmo Lake were allowed to oxidize, and the quantities of leached metals were determined. The total amounts of leached metals were considered to equal several years of leaching in field conditions. If applied on the estimated amount of dredge spoils used in this study, the results from Peltola and Åström (2002) indicates that Larsmo-Öja Lake receives every year 2600, 90, 18 and<1.5 kg of Al, Zn, Ni and Cd, respectively, from dredge spoils. These numbers are roughly only one per mile of the 2,300, 60, 20 and 0.2 t of Al, Zn, Ni and Cd, respectively, that is carried to the lake by the streams and rivers. Even though the acidic metal load produced by dredging operations is insignificant on the lake as a whole, they can still have a significant short-term local effect when dredge spoils in the study area tend to release their acidity at a relatively fast rate.

4.2.2 Effects of hydrology and river discharge on lake water quality

The study shows that the impact from a.s. soils is highly dependent on hydrological conditions. Therefore, spring and autumn months are most affected, when the a.s. soils are intensively flushed. During the spring, a linear drop in pH is prevented as a result of dilution by melt waters compared to the autumn. During winter and summer, pH is normally relatively high, even though some occasional low pH events were also found during these seasons. The normally high pH is logical for the winter season when the ground is normally frozen, which prevents flushing of the a.s. soils. During the summer, the general lack of low pH, despite occasional heavy rainfall, is difficult to explain from the available data. The high evapotranspiration during the summer may cause the soil cracks typical of a.s. soils to widen and

induce preferential flow. This may give the percolating water only limited time to collect acidity and metals from inside soil aggregates (Österholm and Åström, 2008).

Roos and Åström (2005a) found similar elevated concentrations of sulfate and metals typical of a.s. soils in the Esse River, but concluded that the metal load occurred as "hidden" since their analysis showed no detrimentally low pH based on four samplings from the summer of 1999 to the spring of 2000. The data sets on daily pH and specific runoff used in the current study showed, however, that the samplings in Roos and Åström (2005a) were performed during low to moderate runoff events, and that detrimentally low pH occurred, in fact, twice during short periods of high runoff in the autumn 1999 (minimum pH 4.9 and 5.1, Fig. 7), and once during high runoff in the spring of 2000 (minimum pH 5.2, figure not shown). This is a good example of the great temporal variation in the acidic metal discharge, and the difficulties in obtaining enough information about the extent and effects through water sampling. The calculations of the total amounts of sulfuric acid and metals in the previous section were also based on only a few samplings, and the results may therefore also be questionable. However, the daily data on specific runoff and pH indicated that the hydrological conditions during the samplings were representative for the seasons, and in addition, the calculation of a runoff-weighted average should give robust results.

The variations in EC related to runoff are less clear. The EC rose with increasing runoff in November, both in the river and the lake, but the increase seemed to cease at 10 – 20 L s^{-1} km^{-2}. No general variation in EC with increasing runoff could be observed during the other seasons. Especially in Larsmo Lake, both low and high EC occurred in winter and summer during low runoff. This is because the effects of acidic metal discharge in the autumn sometimes lingered in the lake through the winter, while the sometimes high EC during the summer was mainly caused by the high proportion of well-buffered ground water. Notable is that even though the month of May showed among the lowest pH and fairly high Al and sulfate concentrations in the lake, the same month showed among the lowest EC. Consequently, even though EC indicates effects of dilution in the spring, concentrations of ions not related to a.s. soils (e.g. OC) are more affected by dilution than ions typical of a.s. soils.

The common opinion is that dry summers cause enhanced acidic events the following autumn. However, no such clear indications were found in this study. Average specific runoff in the summers 1975 – 2009 was 5.8 L s^{-1} km^{-2}, and several dry summers with an average runoff of 0.29 – 3.8 L s^{-1} km^{-2} did not cause any exceptional low pH the following autumn. However, since high runoff is required for acidity to be flushed to streams, the removal of autumn days with low to moderate runoff (<10 L s^{-1} km^{-2}) from the calculations resulted in a significant correlation in the Esse River, but not for the Larsmo Lake. This may indicate that the lake system is too large to react to the single

events of droughts. Sufficient runoff during autumn was always crucial for the severity of acidic events both in the Esse River and Larsmo Lake. In other words, there always seemed to be a pool of acidity in the a.s. soils waiting to flushed out that, at least in the short run, was not related to extreme summer droughts. Accordingly, pH was more predictable during the spring from previous summer runoff both in the Esse River and Larsmo Lake due to the intensive runoff produced by snow melt. Especially evident in the lake, acidic events after summer droughts often occurred with a delay and spanned over several years, and several subsequent dry summers seemed to enhance the effects. A recent example for the lake is found with the dry summers of 2009 and 2010 (average runoff 0.29 and 4.0 L s^{-1} km^{-2}, respectively) causing low pH in the springs and autumns of 2010 and 2011, and in the spring of 2012. However, exceptions to this have occurred; the dry summer of 2006 caused an acidic event the following autumn even though the summer of 2005 was close to normal (Papers II and III). Also then, several acidic events reoccurred in the lake until spring 2008. The risk of increased enhanced acidic events reoccurring several years after subsequent summer droughts was also found in Österholm and Åström (2008).

The Esse River accounts for almost half of the water discharging into Larsmo-Öja Lake, and shows the generally best water quality of the four studied rivers. The river has therefore a significant role in the quality of the lake water, and often dilutes the more acidic water from the other rivers and low-order streams. But since pH in the Esse River has decreased below 5.5, and even 5.0, quite frequently, the river has also often heavily affected the lake in a negative way. Even though there is great variation in the water quality between the rivers, the relative variance between the rivers is similar, and therefore the vast data on the Esse River acquired from the water plant is suitable for representing variance in impact from a.s. soils (pH and EC) in the total water discharging into the lake (Paper II). It is, however, important to note that the Esse River is regulated upstream at the outlet of the large Lappajärvi Lake (located about 70 m above current sea level) to even out the flow. This is because of the needs of the nine hydro power plants downstream from Lappajärvi Lake, and also due to the prevention of flooding. Therefore, during the rapid increases in runoff during springs and autumns, the flow rate from Lappajärvi Lake that could dilute the discharge from a.s. soils does not increase in the same proportions as the flow downstream. Even though this has no effect on the total input of acidity and metals, the flow regulation may cause momentarily lower pH and higher metal concentrations downstream in the Esse River than otherwise would have been the case. This may also briefly intensify the load on Larsmo-Öja Lake.

Due to the high runoff during the spring, pH declined in Larsmo-Öja Lake at the same rate as in the Esse River. A high proportion of low-buffered melt water may also dilute the buffering capacity and enhance the initial drop in pH during spring (Laudon and Bishop, 1999). During the autumn, runoff is

lower, and initial changes in pH in the discharging river water seemed to be diluted and neutralized in the lake. Sulfate, which is the main anion controlling EC in areas with a significant occurrence of a.s. soils, is a conservative ion and is not affected by buffering reactions. Therefore, EC in the lake responded to changes in EC in the discharging river water more immediately. The lake retention time during the two samplings in autumn 2007, when the combined river water (pH 5.0) was titrated to lake water (pH 5.9 – 6.5), was about 30 days. This shows that any well-buffered lake water could have been replaced with potentially harmful water if the hydrological conditions would have prevailed for a couple of weeks (50 – 67% of river water was needed to lower pH to less than 5.5). However, estimating the rate of decline in water quality is difficult because the lake retention time may vary in the different parts of the lake. Also, the important low-order streams that contribute by about 25% of the acidic load were not included in the test, and may speed up the acidic event. This indicates that the lake is in a constantly vulnerable state, and any increased rate of prolonged autumn rains spanning into winters due to a potential climate change, may cause more frequent severe events with low pH. This may not necessarily increase obvious environmental damage such as visible fish kills, but rather cause, for example, an increased disturbance in the reproduction of autumn and winter spawning fish (Paper II and III). Increased runoff during wintertime is predicted to cause overall deterioration in water quality in areas with a.s. soils (Saarinen and Kløve, 2012). However, a rapid decline in water quality, with immediate results seen as visible fish kills, is possible after extreme summer droughts. The most recent example is the autumn 2006, when pH dropped to 4.1 on November 20th in the Esse River, and an extreme decline in pH was also highly likely in the three smaller rivers and numerous low-order streams. Dead fish were observed in the estuary of the joint mouth of the Esse and the Purmo rivers concurrently with the pH-decline, and about a week later in the whole lake (Paper III). This also indicates that fish are not always able to escape acidic events, even though better water quality is available elsewhere in the lake or despite available escape routes to the sea.

The building of the embankments is often blamed for the acidification and related fish kills in Larsmo-Öja Lake, since no fish kills occurred before the embankments were built. Even though the embankments makes the lake area more vulnerable to the acidic metal discharge by preventing the dispersion of well-buffered brackish water, the underlying reason for the low pH and high metal concentrations is the acidic metal load carried by the rivers and streams. The rivers discharging into the lake became severely acidified at the end of the 1960s (Paper II), which was a common phenomenon in many rivers in western Finland. This was a result of intensive drainage projects at the time (Åström et al., 2005; Saarinen et al., 2010; Suupohja, 1973), which included the installation of effective subsurface pipe-drainage that is known to significantly increase the discharge of acidity and metals compared to

traditional open drains (Palko and Yli-Halla, 1993). The HERTTA data suggests that a severe drop in pH also occurred in Larsmo Lake at this period. Current situations in other estuaries in western Finland (such as the Kyrö River, Hudd and Leskelä (1998)) suggest that even without the embankments the lake area would still have become affected by acidic metal discharge. This is due to the widespread estuary during periods of high runoff and the limited possibilities for fish eggs, larvae and juveniles to escape acidic metal discharge.

4.2.3 Long-term trends

Even though the seasonal and yearly variations in water quality are great, the data on pH and total Al concentrations in the Esse River showed a slow improvement of the water quality that is unrelated to any possible changes in runoff. This may be due to a depletion of the acidic pool in existing a.s. soils. The data from the HERTTA database indicated that the pH in the lake also recovered until the mid-1970s or 1990s, but the data are too irregularly sampled and inconsistent to allow any valid trend tests. Inconsistent long-term data are unfortunately common in the databases for many water courses, and the importance of well planned sampling programs cannot be highlighted enough. The vast data acquired from the paper industry begin in 1975, and provided consistent data for trend analysis. The results showed, somewhat contradictory, that no overall change in pH has taken place 1975 – 2009. However, the 1980s seemed to be most acidic with the exception of the winter months, indicating cold winters, while the winter months show an increase in acidity during the 2000s. The reason why the increased pH in the Esse River does not show in Larsmo Lake may be due to increased acidic load from the three smaller rivers and the numerous low-order streams that compensate for the improved pH in the Esse River. Dissolved metals in the smaller rivers and especially the low-order streams are transported in relatively larger proportions to the lake compared to the Esse River, which the increasing trend in Al concentrations in the lake may confirm. However, April and November, months that are typically heavily affected by discharge from a.s. soils, are the only individual months lacking trends in the Al data from the lake, and the possibly increasing impact from the smaller rivers and low-order streams cannot be confirmed with available data.

The observed increasing trend in EC in the Esse River is somewhat contradictory since a rise in pH and decrease in Al would suggest a lower impact from a.s. soils. Despite that the relationship between pH and EC has changed, the increase in EC is relatively small, and EC is still dominated by discharge from a.s. soils. Thus, data on EC is still considered representative in this study for estimating the impact from a.s. soils. A possible explanation for the rising EC in the river may be that since the sulfidic/sulfuric material in the study area seems to be shallow, deeper flow paths through underlying

non-sulfuric material (increase of elements not associated with a.s. soils) may increase the ionic strength. However, the rising EC cannot be clearly explained by available data.

The results from the trend testing were based on pH and EC taken from the fifteenth of every month, but the same results were obtained using the whole data sets (10^{th} percentiles, medians and 90^{th} percentiles every month). This suggests that in order to study long-term trends of different parameters, sampling once per month (or even once per season) may be enough, provided that the timing is consistent. However, it is important to bear in mind that the study of short-term effects of discharge from a.s. soils may require significantly more frequent sampling because of the extreme temporal variation of the acidic metal discharge.

Present models for a possible climate change predict warmer and rainier winters. The increase in springtime temperature, the earlier spring floods, and the possible increase in acidic events during the cold period in the study area (Paper II and Paper III) may indicate that such events have already occurred more frequently in later years. Because Larmo-Öja Lake is more or less susceptible to low-pH events on a yearly basis, probably often close to the brink of what the current biota can endure, reoccurring prolonged autumn rain spells that reach into winters may cause an increased risk of further deterioration in ecology. Drawn-out acidic events during the winter are considered to have especially serious consequences for autumn and winter spawning fish species (such as the burbot, *Lota lota* L. and whitefish, *Coregonus lavaretus*). Fish that reproduce in late spring or early summer (such as the bream, *Abramis Brama*) will probably benefit if the acidic events during the spring occur earlier due to earlier spring floods (Hudd, pers. comm.). However, as already concluded in the previous section, the deterioration in water quality predicted in areas with a.s. soils due to a possible climate change may cause an overall lowered ecological status (Saarinen and Kløve, 2012).

4.3 Effects of a.s. soils on the occurrence of burbot larvae

Visible fish kills are well noted effects of acid metal discharge. However, less severe acidic events were shown to cause a failure in the reproduction of burbot even though visible fish kills were absent. Although the study on the occurrence of burbot larvae in Larsmo Lake in this work is based on data from only seven years and only two locations, the results showed that a few days of monitoring burbot larvae gave comparable results to several months of frequent pH measurements. Hudd and Kjellman (2002) gained similar results from catch statistics in the estuary of the nearby Kyrö River, but the critical period for reproduction was shown to be somewhat later than in the current study. Fig. 11 suggests that the median pH$\leq$5.8 during the period critical for reproduction of burbot in the Larsmo Lake may cause poor

production of burbot offspring, and the long-term data (1975 – 2009) shows that such events have occurred almost every third year in Larsmo Lake. The fact that two periods proved to be critical for the occurrence of burbot larvae (late autumn to winter and late winter to early spring) may indicate that restrained migration to spawning sites, as well as actual disturbance on egg development, may occur. However, this may also be because of insufficient time for the lake water to be replaced between autumn and spring, and also because of an indirect relation between water quality during the two periods due to soil geochemistry in areas with a.s. soils (Österholm and Åström, 2008). However, no such clear connection between the two critical periods was found (Paper III), and the knowledge as to whether there are, in fact, two periods that are crucial for the reproduction of burbot larvae would need further studies.

Since estuaries in boreal environments are important reproduction areas for fish but, at the same time, susceptible to acidic metal discharge, the simple and inexpensive method to monitor larval communities has the potential to act as a biological indicator in understanding impact from land use, meteorology and climate in areas with a.s. soils with commensurability to coastal water quality and fisheries. Possible biological indicators may prove important since the episodic nature of acidic metal discharge makes it is very difficult to gain correspondent knowledge with only water sampling.

4.4 Acid sulfate soils and acid mine drainage (AMD)

In November 2012, the Talvivaara Sotkamo mine in Finland, mining the world's largest Ni-, Cu-, Zn- and Co mineralization in black shale, gained large-scale attention due to an accidental discharge of about 236,000 m^3 of waste water in just a few days to nearby rivers and lakes. This was described as an acidic metal pulse and caused some fish kills and subsequent massive reactions from the public (Finnish Environment Institute). Estimations of the average concentrations of various metals and ions in the acidic (pH 3) discharging water were extremely high; sulfate- and Ni concentrations were estimated at 12,000 – 24,000 mg/l and 0.5 – 42 mg/l, respectively (Talvivaara supplemental permission application). In the river downstream from the mine, the highest measured Al-, Ni-, Zn- and Cd concentrations were 45, 8.2, 4.0 and 0.009 mg/l, respectively (Talvivaara-blog 2012; YLE-news, 11-14-2012).

Discharge from acid sulfate soils is often compared to AMD because they are both a result of sulfide oxidation causing low pH and elevated concentrations of the same suite of metals. The comparison between the Talvivaara mining accident and the situation in Larsmo-Öja Lake is relevant since the discharge of acidity and metals takes place in lake environments. Even though the concentrations are extremely high in the Talvivaara mining area (the concentrations in the river exceed 1.6 – 41 times the maximum concentrations measured in the low-order streams discharging into the

Larsmo-Öja Lake, Paper I), the total amounts are lower than those that the Larsmo-Öja Lake received in 2007. Approximately 3,200, 720 and 3.2 t of sulfate, Al and Ni, respectively, escaped in the leakage from the Talvivaara mine, while 65,000, 2,300 and 20 t, respectively, were discharged to Larsmo-Öja lake in 2007. In addition to the four rivers and many low-order streams used in the comparison with the AMD, there are a total of about 30 rivers (and vast number of low-order streams) found in western Finland that have been susceptible to elevated metal concentrations during the last 40 years. This study supports the results in Österholm and Åström (2004) and Sundström et al. (2002), who concluded that discharge from a.s. soils is today by far the most severe metal polluter of Finnish water courses.

4.5 Mitigation

Since the main discharge to Larsmo-Öja Lake takes place in the southern part, suggestions have been made to only keep the southern outlet to the sea open during periods of enhanced acidic metal discharge. This would divert the river water immediately to the sea without dispersing to the northern part of the lake, which would create a pocket of better water quality for the biota to temporarily escape to. The dispersion of lake water was investigated by analyzing sulfur isotopes ($\delta^{34}S$) in the water. The results indicated that the southern and middle part of the lake had a similar isotopic composition as the main rivers, and the river water seemed to take the shortest way out of the lake without dispersing to the northern part. This indicates that by only keeping the southern outlet open during severe acidic events, fish have a chance to escape to the north and the fish stocks in the lake would recover more quickly. This method is, however, only considered as a local first-aid measure, and using this will also create more pressure on the environment outside the embankments.

The liming of water courses is a method that often comes into discussion. For the neutralization of atmospheric deposition, the method has been commonly used in Norway and Sweden (Henrikson and Brodin, 1995; Nyberg and Thörnelöf, 1988; Rosseland and Hindar, 1988), and to a lesser extent in Finland (Alasaarela et al., 1990; Iivonen, 1998). The liming of drainage waters from a.s. soils, however, poses more technical challenges mainly due to the low dissolution of the powdered limestone that is commonly used in liming procedures (Weppling, 1993). This requires the building of limestone dosers that automatically reacts on changes in pH, and mixes the limestone effectively in the water to maximize the dissolution of the limestone. In this study, the periods when pH in the Esse River was below 5.5 was used as an indication of a severe threat to Larsmo-Öja Lake, and the limestone requirement was estimated during these events. The required amount of limestone to neutralize all river water during such periods showed potential to rise to hundreds or thousands of t per year. Due to the episodic

nature of the acidic metal discharge, this amount was needed to be distributed during a very limited time; the average daily dosage was in the order of 100 t. If the prize of powdered limestone is about 50 €/t, the yearly cost at such occasions will be 17,000 – 165,000 €. Even though liming may not be required every year, the presented limestone requirements and costs are considered to be greatly underestimated because a) the liming requires the building and maintaining of a network of limestone dosers, which will cause significant additional costs, b) these numbers are based only on the time when pH in the Esse River drops below 5.5 (pH in the other rivers drops more frequently below 5.5), and b) the important low-order streams in the near field that contribute with about 25% of the acidic load were not included in the calculations. In the nearby a.s. soil-affected Kyrö River, the liming of water courses was estimated to a yearly cost of 1 – 5 million € (Rautio et al., 2005). Since the catchment size of Larsmo-Öja Lake (4290 km^2) is somewhat smaller compared to the size of the catchment of the Kyrö River (4923 km^2), and the relative area of a.s. soils is probably smaller (leading to lower acidity), the costs in the current study area can be considered to be somewhat lower, although still substantial. Additional drawbacks connected to the liming of metal rich water courses is the large amount of metal rich precipitates that is created, which may cause further ecological inconvenience. The advantage with this method is that it is reasonably well-tested.

Controlled subsurface pipe-drainage (CPD) has gained popularity on agricultural land underlain with a.s. soils. So far, the technique has unfortunately not shown the desired effects on ground water level or soil- and water geochemistry mainly due to by-pass flow. To prevent this, plastic sheets were installed around a test-field down to a depth of 180 cm. Two of the subfields were forested with no artificial drainage during the sampling in 2009, but showed the same pH, actual acidity and oxidation depth as the subfield that has been in continuous agricultural use. The oxidation depth in all three subfields was lower than the water level in the Purmo River that the field drains into, and even 40 – 70 cm lower than the water level in Larsmo Lake that the Purmo River drains into. This demonstrates the drainage efficiency of evapotranspiration induced by tree growth. Artificial drainage on silty soils, in contrast to clayey sediments (Österholm and Åström, 2004), is therefore not always needed for considerable sulfur oxidation.

Since the installation of CPD requires dry soil conditions, any excess water from the preceding spring could not be stored during the first year of operation in 2009. Successful controlling of the ground water began in 2010, and no obvious changes in pH, oxidation depth or actual acidity were observed three years later, except for an increased pH in the plow layer due to the addition of about 10 t of limestone/ha. Therefore, the installation of a modern effective drainage system on the previously ineffectively drained a.s. soil has not, in the short-term, caused any detectable increase in soil acidity through the successful control of ground water and prevention of by-pass

flow. Controlled subsurface pipe-drainage including the plastic sheets can therefore be recommended when installing a modern drainage system on a.s. soils in order to avoid an increased environmental impact. It is, however, important to note that the farmer or land owner has to actively observe the ground water level, and accordingly adjust the drainage level for the desired effects to take place. It is also important to conduct more long-term studies both on soil- and water geochemistry to conclude the total effects of the technique. Since the spatial geochemical pattern in the rivers shows an increasing input of acidity and metals downstream (below 20 – 60 m above sea level), the main a.s. soil-hotspots are found close to the coast. It is here that focus should be placed when applying mitigation methods, such as CPD with plastic sheets. It is also important to more precisely map occurrences of a.s. soils and sulfidic sediments with the aid of spatial modeling techniques (Beucher et al., 2013) for the effective application of mitigation methods.

The cost for installing CPD with plastic sheets on the 137 km^2 a.s. soils in the study area (Palko and Alasaarela, 1988) is roughly 8.2 million € (600 €/ha, Rainer Rosendahl, pers. comm.). This single cost will likely pay itself back within a decade, or a couple of decades, compared to the previously presented costs associated to liming procedures, and CPD with plastic sheets may be functional for as much as 50 years. The main drawback is, as previously mentioned, that the method is poorly studied and the environmental effects are uncertain.

5. Conclusions

For many years, the reasons for the episodic acidic events and fish kills in the artificially embanked Larsmo-Öja Lake have been debated. This is mainly because the acidification and fish kills started to take place after the building of the embankments, and the brackish water was prevented from diluting and neutralizing the acidity. Even though the embankments may cause the lake area to be more vulnerable to the acidity, this study showed that the main reason for the bad water quality is due to intensive land use on acid sulfate (a.s.) soils, causing the streams and rivers discharging into the lake to become heavily acidified with high metal concentrations. Since the late 1960s this has resulted in large fish kills and declining fish stocks not only in the lake, but also in many rivers and coastal areas in western Finland. The lake and all four studied rivers have experienced severely low pH (pH<5) and high concentrations of dissolved metals more or less on a yearly basis, and the ecological status in the water courses is therefore poor. Other discussed sources of acidity, such as organic acids and dredging operations, were shown to be unimportant. The effects from discharge from a.s. soils on the rivers commonly start to show at 20 – 60 m above sea level with an increasing intensity downstream since the main hotspot areas for a.s. soils are

located close to the coast. Therefore, the numerous small streams in the lake´s near-field were shown to contribute with as much as one fourth of the acidity and one third of the metal load to the lake, even though they drain only 7% of the catchment.

The acidic metal discharge was shown to occur very episodically due to variations in hydrology, with relatively short periods of high runoff during spring and autumn showing most severe water quality. Dry summers that may increase oxidation and acidity were shown to have little immediate impact on water quality. Instead, high acidity was more a result of intensive runoff. A summer drought, especially several subsequent droughts, seemed to cause a rather delayed increase in acidity that spanned for several years after, but was always dependent on intensive runoff.

The main river in the area, the Esse River, has shown a slow but steady recovery in pH since the worst years in the early 1970s, probably due to ongoing depletion of the acidity in the current a.s. soils. Data for the recipient Larsmo Lake were available from 1975, and showed the lowest pH in the 1980s but no overall improved pH in contrast to the Esse River. This could mean that the input of acidic load from the rest of the catchment has increased. Indications that acidic events both in the Esse River and Larsmo Lake became more common during the winters in the 2000s may be related to a potential climate change. Since the acidic metal load is very dependent on high runoff, the increased risk of prolonged rains during the cold season, as current predictions of climate change indicate, may have further serious consequences in the already vulnerable study area. Consistent data is necessary to understand long-term changes in water quality. Unfortunately, the irregular sampling performed by environmental authorities does not benefit such research, and the current monitoring programs should be updated.

Since estuaries are important spawning and nursing areas for fish, the acidic metal surges may have caused frequent failures in the production of burbot offspring as often as almost every third year in Larsmo Lake. This may have larger consequences for fish stocks and fisheries in the long run than the relatively rare visible fish kills. Because of the episodic nature of acidic metal discharge, the full consequences are not likely understood with water sampling. In this study, the simple method of monitoring burbot larvae showed high commensurability to frequent water sampling for several months. Biological indicators, such as monitoring fish larval communities, may therefore prove very important for understanding the connection between land use, climate conditions, water quality in rivers and estuaries and final consequences for coastal fish stocks and fisheries.

Preventing actions, such as avoiding the unnecessary draining of sulfidic sediments, are by far the most important methods to prevent environmental damage. The moment the acidity and metals are released in the soil or into streams, it is often too late or too expensive to take measures. Re-directing

the acidic river water from the Larsmo-Öja Lake only through the southern outlet can only be regarded as a first-aid measure, and the liming of water is challenging due to the enormous amounts of required lime. Controlling the ground water level with controlled subsurface pipe-drainage (CPD) has increased in popularity on a.s. soils, but without showing hardly any environmental effects. In this study, the short-term (three years) period of successful control of the ground water by CPD, with the aid of plastic sheets to prevent by-pass flow, appeared to avoid any harmful increase in soil acidity that conventional pipe-drainage probably would have caused. Increased knowledge of the underlying causes of the acidic metal discharge and understanding the full environmental impact will enable us to apply effective mitigation methods in the right areas for permanently improved water quality.

6. Acknowledgements

I am grateful to my supervisor, associate Prof Peter Österholm, who saw the opportunity to make Larsmo-Öja Lake a subject of a Ph. D. thesis. Peter has provided the knowledge and supervision to make this thesis possible. Thanks to Prof. emeritus Gunnar Jacks, who introduced me to the world of water- and soil science, and provided me the opportunity to write my MSc thesis in the subject. Head of department Prof Olav "Juffi" Eklund and Prof. emeritus Carl Ehlers have my gratitude for the support during my studies. Thanks to Hjalmar Laudon and Pasi Peltola for reviewing my manuscripts and giving suggestions to improve them.

I am grateful to all the help I received from co-authors, colleagues, personnel and students at Åbo Akademi University, and to all those who have provided information and data for my thesis: Sören Fröjdö has often provided useful gadgets for my laboratory work and valuable comments on manuscripts, and helped with my computer work. Richard Hudd broadened my view by introducing me to fish biology. Mats Nylund, Rainer Rosendahl and Markku-Yli Halla made the study of mitigation methods possible. The following people aided me in sampling and analysis: Anton Boman, Simon Dahlström, Anton Grindgärds, Stefan Mattbäck, Mika Siekkinen, Richard Siemssen, Seija Virtanen, Sofia Zittra-Bärlund and Leif Österholm. Valuable information about the study area was provided by the following representatives for environmental authorities: Karin Björkgård, Michael Hagström, Kurt Nyman, Karl-Erik Storberg, Sonja Sundqvist-Pellinen and Jennie Wikström. I thank in particular Jan Snellman at Jakobstad water plant and Kari Saari at UPM-Kymmene paper mill in Jakobstad who provided the data on which a large part of the results in this thesis are based on. Birthe and Ralf Wistbacka have given me chance to distribute my research to broader view. Thanks to Pia Sonck-Koota with the practical help at the institution. I

have missed my friends, colleagues, students and personnel when living in Jakobstad, and I always looked forward to visiting Åbo during the last three years.

I would like to thank my family and friends. My wife Daniela has supported me and commented on countless versions of articles and funding applications, and even helped me in the laboratory and field work. Our lively son Elis has been a healthy distraction from the writing work. I would like to thank my parents, grandparents and sister who have always supported me. My parents-in-law have given me valuable insight in the work of farmers. Thanks to my friends for the great time we had, especially to Roger Backman, who also kindly let me use his apartment in Åbo during the last years.

I am thankful to the following institutions for providing funding for this project: Svenska Litteratursällskapet i Finland: Ingrid, Margit och Henrik Höijers donationsfond II, Österbottens landskapsförbund, Stiftelsen för Åbo Akademi, Otto A. Malms donationsfond, Magnus Ehrnrooths stiftelse, Svenska Österbottens Kulturfond, Svensk-Österbottniska Samfundet r.f., K.H. Renlunds stiftelse, Maa -ja vesitekniikan tuki r.y., Suomen Kulttuurirahaston Etelä-Pohjanmaan rahasto, Rektor för Åbo Akademi.

7. References

Alasaarela, E., Havu, J., Heikkinen, K. & Weppling, K. 1990. Neutralization of acidified watercourses. In: Kauppi, P., Anttila, P., Kenttämies, K. (Eds.). Acidification in Finland. Springer- Verlag. Berlin, Heidelberg, 1117 – 1125.

Andriesse, W., van Meensvoort, M. E. F., 2006. Acid Sulfate Soils: distribution and extent. In: Lal, R (Ed.), Encyclopedia of Soil Science, 2nd edition. Taylor & Francis Group, New York, 14 – 19 (electronic version).

Anonymous., 1896. Fiskepidemi, Fisken i Kyroelf, Hvad går åt fiskarna? Undersökningar i anledning av fiskepidemin i Kyro och Nykarleby elfvar. Fiskeritidskrift för Finland 5, 12 – 14.

Åström, M., 1998. Partitioning of transition metals in oxidized and reduced zones of sulphide-bearing fine-grained sediments. Applied Geochemistry 13 (5), 607 – 617.

Åström, M., 2001. The effect of acid soil leaching on trace element abundance in a medium-sized stream, W. Finland. Applied Geochemistry 16, 387 – 396.

Åström, M., Åström, J., 1997. Geochemistry of stream water in a catchment in Finland affected by sulphidic fine sediments. Applied Geochemistry 12, 593–605.

Åström, M., Björklund, A., 1995. Impact of acid sulfate soils on stream water geochemistry in western Finland. Journal of Geochemical Exploration 55, 163 – 170.

Åström, M., Björklund, A., 1997. Geochemistry and acidity of sulphate-bearing postglacial sediments of western Finland. Environmental Geochemistry and Health 19, 155 – 164.

Åström, M., Spiro, B., 2005. Sources of acidity and metals in a stream draning acid sulphate soil, till and peat, western Finland, revealed by a hydrochemical and sulphur isotope study. Agricultural and Food Science 14, 34 – 43.

Åström, M., Sundström, R., Holmberg, M., Storberg, K.-L., 2005. PH of streams in western Finland – a perspective from the middle ages into the mid 21st century. Agricultural and Food Science 14, 5 – 13.

Backlund, K., Boman, A., Fröjdö, S., Åström, M., 2005. An analytical procedure for determination of sulphur species and isotopes in boreal acid sulphate soils and sediments. Agricultural and Food Science 14, 70 – 82.

Beucher, A., Österholm, P., Martinkauppi, A., Edén, P., Fröjdö, S., 2013, Artificial neural network for acid sulfate soil mapping: Application to the Sirppujoki River catchment area, south-western Finland. Journal of Geochemical Exploration 125, 46 – 56.

Boman, A., Fröjdö, S., Åström, M., 2008. Sulfur dynamics in boreal acid sulfate soils rich in metastable iron sulfide-The role of artificial drainage. Chemical Geology 255, 68 – 77.

Boman, A., Fröjdö, S., Backlund, K., Åström, M.E., 2010. Impact of isostatic land uplift and artificial drainage on oxidation of brackish-water sediments rich in metastable iron sulfide. Ceochimica et Cosmochimica Acta 74, 1268 – 1281.

Burton, E.D., Sullivan, L.A., Bush, R.T., Johnston, S.G., Keene, A.F., 2008. A simple and inexpensive chromium-reducible sulfur method for acid-sulfate soils. Applied Geochemistry 23, 2759 – 2766.

Bydén, S., Larsson, A-M., Olsson, M., 2003. Mäta vatten, Undersökning av sött och salt vatten third ed. Avdelning för tillämpad miljövetenskap och Avdelningen för oceanografi, Göteborgs universitet (in Swedish).

Edén, P., Weppling, K., Jokela, S., 1999. Natural and land-use induced load of acidity, metals, humus and suspended matter in Lestijoki, a river in western Finland. Boreal Environment Research 4, 31 – 43.

Finnish Environment Institute. http://www.syke.fi/en-US/SYKE_Info/Communications_material/Press_releases/Concentrations_of_harmful_metals_have_lo%283359%29. Last accessed 2013-06-09.

Fältmarsch, R., Åström, M., Vuori, K-M., 2008. Environmental risks of metals mobilised from acid sulphate soils in Finland: a litterature review. Boreal Environment Research 13, 444 – 456.

Gensemer, R.W., Playle, R.C., 1999. The bioavailability and toxicity of aluminum in aquatic environments. Critical reviews in environmental science and technology, 29:4 315 – 450.

Geological Survey of Finland. 2013a. http://www.gtk.fi/tietopalvelut/palvelukuvaukset/happamat_sulfaattimaat.html. Last accessed 2013-06-17.

Geological Survey of Finland. 2013b. http://geodata.gtk.fi/Hasu/index.html. Last accessed 2013-06-09.

Haraguchi, A., 2007. Effect of sulfuric acid discharge on river water geochemistry in peat swamp forests in central Kalimantan, Indonesia. Limnology 8, 175 – 182.

Helsel, D.R., Hirsch, R.M., 2002. Statistical Methods in Water Resources. Techniques of Water-Resources Investigations of the United States Geological Survey, Book 4. Hydrologic Analysis and Interpretation, Chapter A.3.

Henrikson, L., Brodin, Y.W. (eds.). 1995. Liming of acidified surface waters: A Swedish syntesis. Springer-Verlag. Berlin-Heidelberg. 458 p.

HERTTA database, 2012. OIVA-environmental Information System at the Centre for Economic Development, Transport and the Environment in Finland. http://wwwp2.ymparisto.fi/tietoapalvelusta.html. Last accessed 2012-11-27.

Hildén, M., Rapport, D., 1993. Four centuries of cumulative impacts on a Finnish river and its estuary: an ecosystem health-approach. Journal of Aquatic Ecosystem Health 2, 261 – 275

Hirsch, R., Alexander, R., Smith, R., 1991. Selection of methods for the detection and estimation of trends in water quality. Water Resources Research 27, 803 – 813.

Hudd, R., 2000. Springtime episodic acidification as a regulatory factor of estuary spawning fish recruitment. Department of Limnology and Environmental Protection University of Helsinki, Finland and Finnish Game and Fisheries Research Institute. Academic dissertation.

Hudd, R., Ahlqvist, J., Blom, A., 2007. Potentiella yngelproduktionsområden för lake och gös i Larsmo- och Öjasjön. Vilt- och fiskeriforskningsinstitutet 2007.

Hudd, R., Kjellman, J., 2002. Bad matching between hatching and acidification: a pitfall for the burbot, Lota lota, off the river Kyrönjoki, Baltic Sea. Fisheries Research 55, 153 – 160.

Hudd, R., Leskelä, A., 1998. Acidification-induced species shifts in coastal fisheries off the river Kyrönjoki, Finland: a case study. Ambio 27, 535 – 538.
¨

Hsieh, Y.P., Shieh, Y.N., 1997. Analysis of reduced inorganic sulfur by diffusion methods: improved apparatus and evaluation for sulfur isotopic studies. Chemical Geology 137, 255 – 261.

Hsieh, Y.P., Yang, C.H., 1989. Diffusion methods for the determination of reduced inorganic sulfur species in sediments. Limnology and Oceanography 34, 1126 – 1130.

Hyne, R.V., Wilson, S.P., 1997, Toxicity of acid-sulphate soil leachate and aluminium to the embryos and larvae of Australian bass (Macquaria Novemaculeata) in estuarine water. Environmental Pollution 97, 221 – 227.

Iivonen, P., 1998. Happamoituneiden vesistöjen kalkitus. Suomen ympäristökeskus. Ympäristöopas 3. 55 s. + liitteet (in Finnish).

Kalliolinna, M., 1996. Luodon-Öjanjärven vedenlaatu vuosina 1989 – 1995. The Association of Water Protection in Western Finland (in Finnish). 52 p.

Kjellman, J., Hudd, R., Leskelä, A., Salmi, J., Lehtonen, H., 1994. Estimation and prognosis of recruitment failures due to episodic acidifications on burbot (Lota lota L.) of the river Kyrönjoki. Aqua Fennica 24, 51 – 57.

Känsälä, L., Björkgård,K., 2002. Helhetsplanen för Kronoby å. Del I: Redogörelse för planen. Västra Finlands miljöcentral. Regionala miljöpublikationer 254 (in Swedish).

Lahermo, P., Väänänen, P., 1996. Geochemical mapping at the Geological Survey of Finland stream waters and stream sediments. Vesitalous 5, 19 – 26 (in Finnish).

Laudon, H., Bishop, K., 1999. Quantifying sources of acid neutralization capacity depression during spring flood episodes in Northern Sweden. Environmental Pollution 105, 427 – 435.

Laudon, H., Köhler, S., Bishop, K.H., 1999. Natural acidity or anthropogenic acidification in the spring flood of northern Sweden? The Science of the Total Environment 234, 63 – 73.

Lehtonen, H., Hudd, R., 1990. The importance of estuaries for the reproduction of freshwater fish in the Gulf of Bothnia. In: van Densen, W.L.T., Steinmetz, B., Hughes, R.H. (Eds.) Management of freshwater fisheries. Proceedings of a symposium organized by the European Inland Fisheries Advisory Commission, Göteborg, Sweden, 31 May-3 June 1988. Pudoc. Wageningen, 82 – 89.

Macdonald, B.C.T., Smith, J., Keene, A.F., Tunks, M., 2004. Impacts of runoff from sulfuric soils on sediment chemistry in an estuarine lake. Science of the Total Environment 329, 115 – 130.

Mattsson, T., Kortelainen, P., Lepistö, A., Räike, A., 2007. Organic and minerogenic acidity in Finnish rivers in relation to land use and deposition. Science of the Total Environment 383, 183 – 192.

McCahon, C.P., Brown, A.F., Poulton, M.J., Pascoe, D., 1989. Effects of acid, aluminium and lime additions on fish and invertebrates in a chronically acidic Welsh stream. Water, Air, and Soil Pollution 45, 345 – 359.

Nordmyr, L., Boman, A., Åström, M., Österholm, P., 2006. Estimation of leakage of chemical elements from boreal acid sulphate soils. Boreal Environmental Research 11 (4), 261 – 273.

Nordmyr, L., Österholm, P., Åström, M., 2008. Estuarine behaviour of metal loads leached from coastal lowland acid sulphate soils. Marine Environmental Research 66, 378 – 393.

Nyberg, P., Thörnelöf, E., 1988. Operational liming of surface waters in Sweden. Water, Air and Soil Pollution 41, 3 – 16.

Nystrand, M., 2012. Element speciation and behavior in metal-rich Boreal river and estuarine systems using ultrafiltration and chemical modeling. Åbo Akademi University. Academic dissertation.

Nystrand, M.I., Österholm, P., 2013. Metal species in a Boreal river system affected by acid sulfate soils. Applied Geochemistry 31, 133 – 141.

Nystrand, M.I., Österholm, P., Nyberg, M., Gustafsson, J.P., 2012. Metal speciation in rivers affected by enhanced soil erosion and acidity. Applied Geochemistry 27, 906 – 916.

Österholm, P., Åström, M., 2002. Spatial trends and losses of major and trace elements in agricultural acid sulphate soils distributed in the artificially drained Rintala area, W. Finland. Applied Geochemistry 17, 1209 – 1218.

Österholm, P., Åström, M., 2004. Quantification of current and future leaching of sulfur and metals from Boreal acid sulfate soils, western Finland. Australian Journal of Soil Research 42, 547 – 551.

Österholm, P., Åström, M., 2008. Meteorological impacts on the water quality in the Pajuluoma acid sulphate soil area, W. Finland. Applied Geochemistry 23, 1594 – 1606.

Österholm, P., Virtanen, S., Uusi-Kämppä, J., Rosendahl, R., Westberg, V., Mäensivu, M., Ylivainio, K., Yli-Halla, M., Turtola, E., 2012. Minimizing sulfide oxidation on acid sulfate farmlands by enhanced controlled drainage and subsurface irrigation. In: Österholm, P., Yli-Halla, M,. Edén, P (Eds.). Proceedings of the 7th International Acid Sulfate Soil Conference, Vaasa, Finland, 2012. Geological Survey of Finland, Guide 56, 166 – 168.

Palko, J., 1994. Acid sulphate soils and their agricultural and environmental problems in Finland. Acta Univ. Oul. C 75, University of Oulu, Academic dissertation.

Palko, J., Alasaarela, E., 1988. Larsmo-Öjasjöns flodområde: Förekomst av sura sulfatjordar och deras inverkan på vattnets surhet (in Swedish). Valtion teknillinen tutkimuskeskus, Oulu.

Palko, J., Räsänen, M., Alasaarela, E., 1987. Luodon-Öjanjärven valuma-alueen maaperän ja vesistön happamuuskartoitus. The survey of the soil and water acidity in the catchment area of Luodon-Öjanjärvi. Vesi- ja ympäristöhallinnon julkaisuja, 11 (in Finnish).

Palko, J., Weppling, K., 1994. Lime requirement experiments in acid sulphate soils. Acta Agriculturae Scandinavica Section B, Soil Plant Science 44, 149 – 156.

Palko, J., Yli-Halla, M., 1988. Solubility of Co, Ni and Mn in some extractants in a Finnish acid sulphate soil area. Acta Agriculturae Scandinavica 38, 153 – 158.

Palko, J., Yli-Halla, M., 1990. Solubility of Al, Cr, Cu and Zn in soils from a Finnish acid sulphate soil area. Acta Agriculturae Scandinavica 40, 117 – 122.

Palko, P., Yli-Halla, M., 1993. Assessment and management of acidity release upon drainage of acid sulphate soils in Finland. Selected Papers of the Ho Chi Minh City Symposium on Acid Sulphate Soils, Wageningen, Netherlands, 411 – 418.

Peltola, P., Åström, M., 2002. Concentrations an leachability of chemical elements in estuarine sulfur-rich sediments, W. Finland. The Science of the Total Environment 284, 109 – 122.

Poléo, A.B.S. 1995. Aluminium polymerization — a mechanism of acute toxicity of aqueous aluminium to fish. Aquatic Toxicology 31, 347 – 356.

Poléo, A.B.S., Østbye, K., Øxnevad, S.A., Anderson, R.A., Heibo, E., Vollestad, L.A. 1997. Toxicity of acid aluminum-rich water to seven freshwater fish species: a comparative laboratory study. Environmental Pollution 96, 129 – 139.

Rask, M., Mannio, J., Forsius, M., Posch, M., Vuorinen, P.J., 1995. How many fish populations in Finland are affected by acid precipitation? Environmental Biology of Fishes 42, 51 – 63.

Rautio, L.M., Aaltonen, E-K., Storberg, K-E., 2006. Preliminärt skötselprogram för Kyrö älvs vattendragsområde. Västra Finlands miljöcentral. Regionala miljöpublikationer 419 (in Finnish and Swedish).

Reimann, C., Filzmoser, P., 1999. Normal and lognormal data distribution in geochemistry: death of a myth. Consequences for the statistical treatment of geochemical and environmental data. Environmental Geology 39 (9), 1001 – 1014.

Roos, M., Åström, M., 2005a. Seasonal and spatial variations in major and trace elements in a regulated boreal river (Esse River) affected by acid sulphate soils. River Research and Applications 21, 351 – 361.

Roos, M., Åström, M., 2005b. Hydrogeochemistry of rivers in an acid sulphate soil hotspot area in western Finland. Agricultural and Food Science 14, 24 – 33.

Rosseland, B.O., Eldhuset, T.D., Staurnes, M., 1990. Environmental effects of aluminium. Environmental Geochemistry and Health 12, 17 – 27.

Rosseland, B.O., Hindar, A., 1988. Liming of lakes, rivers and catchments in Norway. Water, Air and Soil Pollution 41 (1 – 4), 165 – 188.

Saarinen, T.S., Kløve, B., 2012. Past and future seasonal variation in pH and metal concentrations in runoff from river basins on acid sulphate soils in Western Finland. Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering 47:11, 1614 – 1625.

Saarinen, T., Vuori, K.M., Alasaarela, E., Kløve, B., 2010. Long-term trends and variation of acidity, COD_{Mn} and colour in coastal rivers of Western Finland in relation to climate and hydrology. Science of the Total Environment 408, 5019 – 5027.

Sammut, J., Melville, M.D., Callinan, R.B., Fraser, G.C., 1995. Estuarine Acidification: Impacts on Aquatic Biota of Draining Acid Sulphate Soils. Australian Geographical Studies 33, 89 – 100.

Sayer, M.D.J., Reader, J.P., Dalziel, T.R.K., 1993. Freshwater acidification: effects on the early life stages of fish. Reviews in Fish Biology and Fisheries 3, 95 – 132.

Snickars, M., Wistbacka, R., 2000. De kustnära småvattendragens status som fiskeplatser i Österbotten 1997 – 1998 (in Swedish). Jord- och skogsbruksministeriet. Fisk- och viltförvaltningens publikationer 48a/2000 (in Swedish).

Soil Survey Staff., 2010. Keys to soil taxonomy, USDS 11th edition: Natural Resources Conservation Service. 338 p.

Sundström, R., Åström, M., Österholm, P., 2002. Comparison of the metal content in acid sulfate soil runoff and industrial effluents in Finland. Environmental Science & Technology 36, 4269 – 4272.

Sutela, T., Vuori, K-M., Louhi, P., Hovila, K., Jokela, S., Karjalainen, S.M., Keinänen, M., Rask, M., Teppo, A., Urho, L., Vehanen, T., Vuorinen, P.J., Österholm, P., 2012. Happamien sulfaattimaiden aiheuttamat vesistövaikutukset ja kalakuolemat Suomessa. Suomen ympäristö 14. Suomen ympäristökeskus (in Finnish).

Suupohja, O., Erviö, R., Pälikkö, E., Sumari, O., Vuoristo, H., 1973. Selvitys Kyrönjoen ja sen edustan merialueen kalakuolemien syistä. National Board of Waters in Finland (in Finnish).

Talvivaara-blog, 2012. http://suomenluonto.blogit.fi/talvivaara-antoi-kipsisakka-altaan-vuodosta-selityksen/. Last accessed 2013-06-09.

Talvivaara supplemental permission application: http://www.talvivaara.com/files/talvivaara/Ymp%20Taydennys%20/Lupahakemuksen_taydennys_15_2_2013.pdf. Last accessed 2013-06-09.

Tuttle, M.L., Goldhaber, M.B., Williamson, D.L., 1986. An analytical scheme for determining forms of sulphur in oil shales and associated rocks. Talanta 33, 953 – 961.

Ulrich, G.A., Krumholz, L.R., Suflita, J.M., 1997. A rapid and simple method for estimating sulfate reduction activity and quantifying inorganic sulfides. Applied and Environmental Microbiology 63, 1627 – 1630.

Virtanen, S., Simojoki, A., Knuutila, O., Yli-Halla, M., 2013. Monolithic lysimeters as tools to investigate processes in acid sulphate soil. Agricultural Water Management 127, 48 – 58

Vuori, K-M., Mitikka, S., Vuoristo, H., 2009. Classification of the Ecological Status of Surface Waters in Finland. Environmental Guide, 3. Finnish Environment Institute.

Vuorinen, P.J., Keinänen, M., Peuranen, S., Tigerstedt, C., 1999. Effects of iron, aluminium, dissolved humic material and acidity on grayling (Thymallus thymallus) in laboratory exposures, and a comparison of sensitivity with brown trout (Salmo trutta). Boreal Environment Research 3, 405 – 419.

Vuorinen, V., Vuorinen, P., Hoikka, J., Peuranen, S., 1993. Lethal and sublethal threshold values of aluminium and acidity to pike (Esox lucius), whitefish (Coregonus lavaretus pallasi), pike perch (Stizostedion lucioperca) and roach (Rutilus rutilus) yolk-sac fry. The Science of the Total Environment, Supplement, 953 – 967.

Willett, I.R., Melville, M.D., White, I., 1993. Acid drainwaters from potential acid sulfate soils and their impact on estuarine ecosystems. International Institute for Land Reclamation and Improvement Publication 53, 419 – 425.

Waring, C.P., Brown, J.A. 1995. Ionoregulatory and respiratory responses of brown trout, Salmotrutta, exposed to lethal and sublethal aluminium in acidic soft waters. Fish Physiology and Biochemistry 14, 81 – 91.

Weppling, K., 1993. Hydrochemical factors affecting the neutralization demand in acid sulphate waters. Vatten 49, 161 – 170.

Witters, H.E., 1998. Chemical speciation dynamics and toxicity assessment in aquatic systems. Ecotoxicology and Environmental Safety 41, 90 – 95.

Witters, H.E., van Puymbroeck, S., Vangenechten, J.H.D., Vanderborght, O.L.J. 1990. The effect of humic substances on the toxicity of aluminium to adult rainbow trout, *Oncorhynchus mykiss* (Walbaum). Journal of Fish Biology 37, 43 – 53.

Wu, X., Wong, Z.L., Sten, P., Engblom, S., Österholm, P., Dopson, M., 2013. Microbial community potentially responsible for acid and metal release from an Ostrobothnian acid sulfate soil. FEMS Microbiology and Ecology. DOI 10.1111/1574 – 6941.12084

YLE-news: http://areena.yle.fi/tv/1742312. Last accessed 2013-06-09.

Yli-Halla, M., Puustinen, M., Koskiaho, J., 1999. Area of cultivated acid sulfate soils in Finland. Soil Use Manage. 15, 62 – 67.

ISBN 978-952-12-2956-5